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RUBBER CHEMISTRY

AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY





KOSMOS 60

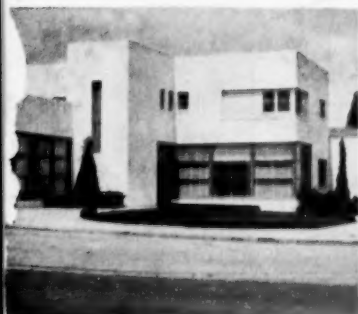
Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil, and its manufacture is scientifically controlled to meet the highest standards. Its superb processing and balance of strength make for the best in rubber products.

UNITED CARBON COMPANY, INC.

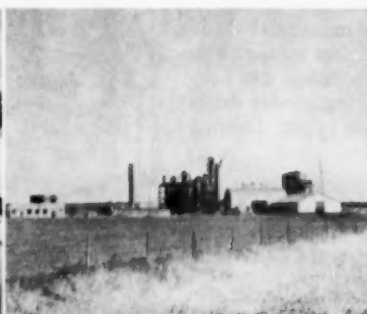
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DYNAMIC GROWTH in Carbon Blacks... *by* WITCO-CONTINENTAL



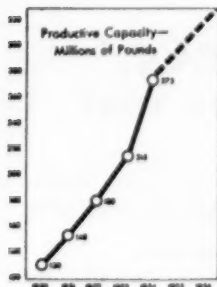
Active Center of Carbon Black Research is the WITCO-CONTINENTAL Laboratory at 1400 W. 10th Avenue, Amarillo, Texas.



Modern Production Facilities, such as this new plant at Ponca City, Oklahoma, enable WITCO-CONTINENTAL to produce a complete line of carbon blacks. Latest process controls assure rigorous uniformity of grades in all 5 WITCO-CONTINENTAL plants.



New Technical Service Laboratory at 213 West Bowery Street, Akron, is completely equipped to handle customers' formulation problems.



Production, research and technical service have shared in the dynamic, yet balanced, growth of WITCO-CONTINENTAL as a producer of carbon blacks.

As our production grows, we are continually expanding our services to provide rubber manufacturers with every benefit of modern carbon black technology.

Call on WITCO-CONTINENTAL for prompt sales and technical service in carbon blacks.

Witco-Continental CARBON BLACKS

FURNACE BLACKS

Continex® SRF — Semi-Reinforcing
 Continex SRF-NS — Non-Staining
 Continex HMF — High Modulus
 Continex HAF — High Abrasion
 Continex FEF — Fast Extruding
 Continex ISAF — Intermediate Super Abrasion
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CHANNEL BLACKS

Continental® AA — (EPC) — Witco No. 12
 Continental A — (MPC) — Witco No. 1
 Continental F — (HPC) — Witco No. 6
 Continental R-40 — (CC) — Conducting

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36 Years of Growth

Use the right **PHILBLACK®** in your rubber recipes!

There are four Philblacks to choose from—just tell us your specific needs. Resilience . . . abrasion resistance . . . low heat buildup . . . high hot tensile? The right Philblack in your recipe can help you achieve these *and many other* desirable characteristics in your finished product.

Manufacturers of rubber products are invited to use Phillips technical sales service facilities for assistance in solving processing problems, too.

Make full use of our valuable scientific data on rubber compounding and performance. For further information on how you can benefit by using Philblack, consult our technical representative.



Meet the Philblacks! **KNOW WHAT THEY'LL DO FOR YOU!**

A**Philblack A FEF Fast Extrusion Furnace Black**

Ideal for smooth tubing, accurate molding, satiny finish. Mixes easily. High, hot tensile. Disperses heat. Non-staining.

I**Philblack I ISAF Intermediate Super Abrasion Furnace Black**

Superior abrasion resistance at moderate cost. Very high resistance to cuts and cracks. More tread miles at high speeds.

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For long, durable life. Good electrical conductivity. Excellent flex. Fine dispersion.

E**Philblack E SAF Super Abrasion Furnace Black**

Toughest black on the market. Extreme abrasion resistance. Withstands aging, cracking, cutting and chipping.



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Export Sales: 80 Broadway, New York 5, N. Y.

West Coast: Harwick Standard Chemical Company, Los Angeles, California.

Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (6-2), Section 3440, P. L. and R. of 1948, authorized September 25, 1940.

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MERAC[®]


A LIQUID ACCELERATOR FOR LATEX—
NATURAL and
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*Merac Offers
these Advantages:*

1. It is a liquid accelerator which upon dilution with water is added directly to latex.
2. It is faster curing at room and elevated curing temperatures than most accelerators.
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 SIMPLIFIES LATEX COMPOUNDING

 ADD DIRECTLY TO LATEX

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PRODUCT
DESERVES**

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Rubber Yellow GD	Rubber Blue GD
Rubber Green FD	Rubber Orange OD

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In Canada contact: Du Pont Company of Canada Limited,
Box 660, Montreal.



Photo courtesy Bettle Rubber Company, Whittier, California

A case of joint enterprise!

Uncontrolled, a string of many joints of drill pipe is surprisingly flexible — rubs and slams against the casing — causes undue wear and damage.

As protectors, drillers first collared the pipe with spacers of natural rubber. These did an excellent job in the face of extreme abuse and abrasion.

But oil-based drilling muds brought a new problem: the natural rubber quickly swelled and deteriorated.

To meet the need for high tensile strength plus resistance to the abrasion and attack of the drilling fluids, an enterprising specialty molding company worked jointly with all concerned to perfect a new compound based on CHEMIGUM — the easy processing nitrile rubber.

The oil resistance of CHEMIGUM made possible a truly "all purpose" protector which not only wears well and retains its position on the pipe, but does so at higher temperatures than any other on the market.

How can the processability, unusual oil resistance and excellent physical properties of CHEMIGUM improve your product? For details, write:

Goodyear, Chemical Division, Akron 16, Ohio



Rubber &
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... an economical vulcanizing agent for heat-resistant, non-blooming stocks

VA-7 is a new liquid vulcanizing agent for all types of unsaturated elastomers. It provides economical "sulfurless" cures for nitrile, GR-S and natural rubber stocks.

Stocks compounded with VA-7 display an outstanding combination of heat aging resistance . . . high tensile strengths . . . good hot compression set resistance . . . and non-blooming characteristics in the cured and uncured states.

VA-7 also offers processing advantages—it can be dispersed more easily and uniformly than sulfur. Stable emulsions for curing latices can easily be prepared from VA-7.

The moderate price of VA-7 is another feature that makes this product worth your investigation. Try VA-7 for heat-resistant, non-blooming stocks at reasonable cost!

For compounding information and a sample of VA-7 fill out and mail the handy coupon.

CHECK LIST OF VA-7 PROPERTIES

- Outstanding heat aging resistance
- Non-blooming in cured or uncured state
- High strengths at low concentrations
- Easy and uniform dispersion
- Good hot compression set
- Moderate price

THIokol CHEMICAL CORPORATION
780 N. Clinton Avenue
Trenton 7, New Jersey

Please send me compounding information ☐
and a sample of VA-7 ☐

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780 NORTH CLINTON AVENUE • TRENTON 7, NEW JERSEY

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We're Expanding Our Plant

to make more Philprene®





Because of greatly increased customer demand for our polymers and masterbatches, Phillips has launched an expansion program to provide an additional 20,000 long tons annually of the more than 20 different types of synthetic rubber materials bearing the PHILPRENE trademark.

Phillips will expand the capacity of its Plains co-polymer plant by 37 per cent to meet the growing rubber needs. A substantial portion of this additional production is expected to become available in the second half of 1956.

Consult our Technical Representative about your particular rubber needs. We like to help our customers make better products . . . and better profits.

CURRENT PHILPRENES

Each is comparable to former GR-S with the same numerical designation except 1605 and 1803 as noted below.

			
HOT	PHILPRENE 1000 PHILPRENE 1001 PHILPRENE 1006 PHILPRENE 1009	PHILPRENE 1010 PHILPRENE 1018 PHILPRENE 1019 NOTE: PHILPRENE	
COLD	PHILPRENE 1500 PHILPRENE 1502 PHILPRENE 1503	1019 AND 1503 ARE ESPECIALLY DESIGNED FOR THE WIRE AND CABLE INDUSTRY	PHILPRENE 1601 PHILPRENE 1605* *Philblack A cold rubber masterbatch
COLD OIL EXTENDED	PHILPRENE 1703 PHILPRENE 1706 PHILPRENE 1708	PHILPRENE 1712	PHILPRENE 1803 similar to GR-S 1801 but incorporating 25 parts Philrich 5

PHILLIPS CHEMICAL COMPANY

Rubber Chemicals Division

318 Water Street, Akron 8, Ohio





...help when needed

You've got a problem by the tail if your competition is gaining advantage over you by manufacturing at lower cost without decreasing quality. Sid Richardson Carbon Co. **TEXAS "E"** and **TEXAS "M"** channel blacks can give you a helping hand toward lowering your costs either when used alone or in blends with higher priced blacks.

TEXAS CHANNEL BLACKS are manufactured in the world's largest channel black plant with our own natural resources nearby, assuring continuing deliveries to fill our customers' requirements.



Sid Richardson
CARBON CO.

FORT WORTH, TEXAS

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ARLON, N. DAKOTA

*Looking for a cost cutting,
quality building
miracle additive?*

USE **VELSICOL**

*hydrocarbon resins
to make better rubber
products, build
quality and cut costs!*



Here are the facts!

PHYSICAL PROPERTIES	GE-9	AB-11-4	X-30
Type	Thermoplastic Hydrocarbon Solid or Powder	Thermoplastic Hydrocarbon Solid or Flaked	Thermoplastic Hydrocarbon Solid or Flaked
Form			
Specific Gravity @ 60°F	1.13-1.15	1.09-1.02	—
Weight per gallon @ 60°F (lbs.)	9.41-9.58	9.08-9.33	—
Bulking Value @ 60°F	0.1044-0.1052	0.1074-0.1102	—
Softening Point (Ball and Ring)	220°-230°F	220°-230°F	210°-220°F
Color (Coal Tar Scale)	20-22	3½-4½	1½-2*
Acid No.	0-2	0-2	0-2
Saponification No.	0-2	0-2	0-2

*Color: Gardner: 10-11; Rosin Scale: I-K.

These resins also have exceptionally good electrical insulation properties, because they are hydrocarbon polymers. Compatible with a variety of natural and synthetic rubber compounds.

FOR: battery cases, electrical insulation, rubber shoe soles and heels, rubber floor tiling, gaskets and jar rings, hard rubber compounds, tubular compounds, mechanical goods, rubber adhesives and cements, reclaimed rubber, molded rubber products, colored rubber stocks.

ADVANTAGES: better milling, calendaring, and tubing; more uniform cures, non-scorchy stocks; greater toughness, hardness, resistance to tearing, aging and abrasion; improved tensile strength and elongation; lower raw materials costs.

Write for
Technical Bulletin 218.

VELSICOL
CHEMICAL CORPORATION

Dept. 96 330 East Grand Ave., Chicago 11, Illinois

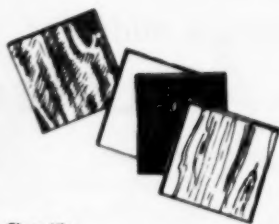


PANAREZ HYDROCARBON RESINS

improve products like these:



Shoe soles

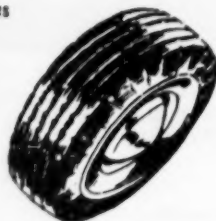


Floor tile

Wire covering



Tires



If you compound rubber it will pay you to investigate *low cost* PANAREZ hydrocarbon resins. These softeners are available in any color from Barrett No. 1 to 18, and softening point from 40° F to 300° F. They are supplied in flaked or solid form.

Compounds containing Panarez resins show **IMPROVED COLOR AND COLOR STABILITY . . . IMPROVED EXTRUDABILITY . . . IMPROVED FLEX CRACK PERFORMANCE and ABRASION RESISTANCE . . . IMPROVED OZONE RESISTANCE . . . IMPROVED TEAR RESISTANCE, TENSILE STRENGTH and ELONGATION.**

No change in compounding technique is required when switching to Panarez resins.

For confidential information about how these low cost resins might be helpful in your business, write us, telling the intended application.



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555 FIFTH AVENUE, NEW YORK 17, N. Y.



PANAPOL
Hydrocarbon drying oils

PANASOL
Aromatic solvents

How long did it take . . . to get from here . . . to here?



Answer: 25 years

With the introduction of hot water heaters in 1926 cars, motorists were beginning to roll in solid comfort during cold winter months. But research and development didn't stop there. Since 1951, air conditioning, at the touch of a button, provides year-round spring temperatures despite weather extremes.

At the same time, the rubber industry was discovering new ways of making its products more versatile and longer lasting. Monsanto has played an important role in this development with its increasing number of rubber chemical products.

For example, Santocure NS, the newest Monsanto accelerator of the sulfenamide type, is characterized by even more delayed action, greater strength and full activity at curing temperatures. As an analogue of regular Santocure it is designed to meet the needs of present day high-speed production which involves high processing temperatures.

For your copy of catalog "Chemicals for the Rubber Industry," write MONSANTO CHEMICAL COMPANY, Rubber Chemicals Dept., 920 Brown St., Akron 11, Ohio.

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Santaflex® F3
Santaflex® AW
Santawhite® Crystals
Santawhite® MX
Santawhite® L
Santawhite® Powder

ALDEHYDE AMINE ACCELERATORS

A-32®
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for highest quality
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HIGH ABRASION OIL FURNACE BLACK

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At same channel black prices, Vulcan 3 gives up to 20% superior roadwear to channel blacks in all types of rubber, plus better-than-channel black flex cracking resistance, mixing time, processing, extrusion, die swell and rate of cure, so change from channel blacks to Vulcan 3 NOW.

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Proved superior to channel blacks in more than 3,500,000 Cabot tire miles of road tests. . . available for Pounds Sterling, Canadian Dollars, or U. S. Dollars.



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NAUGATUCK supplies a complete line of proven accelerators, activators, anti-oxidants, and special chemicals to give you thorough control of rubber product manufacture and performance.

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DDM — modifier

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Write, on your letterhead, for technical data or assistance with any Naugatuck product.

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Naugatuck Chemical

Division of United States Rubber Company
Naugatuck, Connecticut

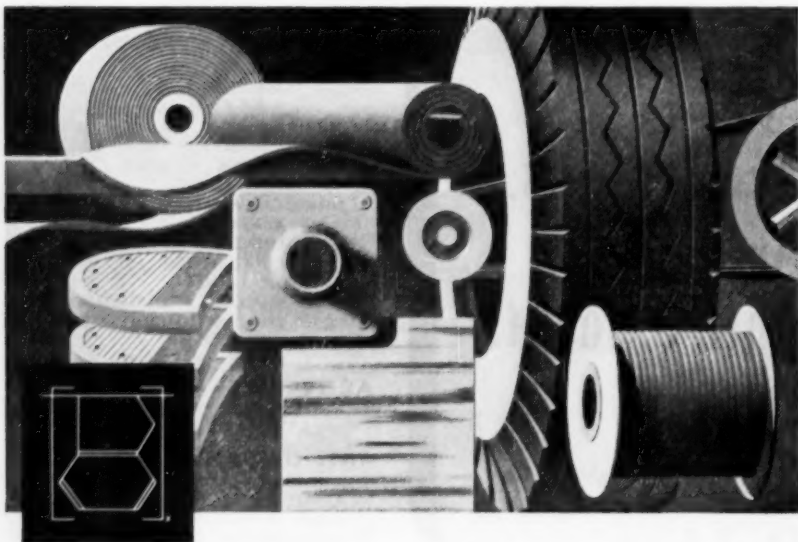


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Coumarone-indene resins by Neville have become standard in the processing of rubber for an ever-increasing variety of products in ever-greater volume throughout the years. Here's why. Users find that Neville gives them constant good quality and fast service, and they save production time and costs and produce better products when they use coumarone resins. Also, Neville has a broad variety of these ideal extender-plasticizers in various grades and melting points to suit every product need. Our chemists will gladly

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NEOPRENE WHV	SUNDEX-53	Cost of compounds comparable to low-cost elastomers.
REGULAR NEOPRENES and NATURAL RUBBER	CIRCO LIGHT RUBBER PROCESS-AID	True softening by physical changes in rubber structure. Large quantities absorbed without blooming.

To learn more about using Sun Rubber Process Aids to get better physicals, lower costs, and easier processing, see your Sun representative. Or write for your copy of Sun's latest Technical Bulletin describing any of the above products. Address **SUN OIL COMPANY, Philadelphia 3, Pa., Dept. RC-1.**

INDUSTRIAL PRODUCTS DEPARTMENT

SUN OIL COMPANY

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IN CANADA: SUN OIL COMPANY, LTD., TORONTO AND MONTREAL

JANUARY - MARCH • 1956

VOLUME XXIX

NUMBER ONE

RUBBER CHEMISTRY

AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY



CARBON BLACKS

for RUBBER COMPOUNDING

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STATEX®125

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STATEX-R

MPC (Medium Processing Channel)
STANDARD MICRONEX®

EPC (Easy Processing Channel)
MICRONEX W-6

FF (Fine Furnace)
STATEX-B

FEF (Fast Extruding Furnace)
STATEX-M

HMF (High Modulus Furnace)
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New York 17, N.Y.



RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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All applications to become Members of Associates of the Division of Rubber Chemistry, with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, George E. Popp, Phillips Chemical Co., 318 Water St., Akron 8, Ohio.

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FUTURE MEETINGS

Meeting	City	Hotel	Date
1956 Spring	Cleveland	Cleveland	May 16-18
1956 Fall	Atlantic City	Chalfonte-Haddon Hall	September 19-21
1957 Spring*	Montreal	Sheraton-Mt. Royal	May 15-17
1957 Fall	New York	Commodore	September 11-13
1958 Spring	Cincinnati	Netherlands Plaza	May 14-16
1958 Fall	Chicago	Sherman	September 10-12
1959 Spring	Buffalo	Statler	May 13-15
1959 Fall	Atlantic City	**	September 16-18

* Joint meeting with the Rubber Division of the Canadian Institute of Chemistry.

** Hotel not yet assigned by the American Chemical Society.

CHARLES GOODYEAR MEDAL AWARD FOR 1956

To all members of the Division of Rubber Chemistry:

This letter is to solicit proposals for candidates for the Charles Goodyear Medal Award for nomination by the Medal Committee at the Spring meeting to be held in Cleveland, May 16-18, 1956.

Your proposals should be presented in the form suggested by the attached *Outline for Proposal*, and mailed to the Division Secretary, Dr. Neal, so as to reach him not later than March 26, 1956.

For your guidance, I am attaching a list of the Charles Goodyear Medalists, together with a list of fields not yet fully recognized. Additional awards in fields already recognized, e.g., polymerization and vulcanization, are, of course, in order. The By-Laws do not prohibit the election of a foreign chemist.

I hope each one of you will consider this matter carefully.

J. M. Ball, Chairman
Charles Goodyear Medal Committee

OUTLINE FOR PROPOSAL OF A CANDIDATE FOR THE CHARLES GOODYEAR MEDAL AWARD

1. Name of candidate.....
2. Statement of contribution of candidate for use for the Award Citation.....
3. General statement concerning the importance of such contribution.....
4. Pertinent publication of the candidate.....
5. Brief biography of the candidate.....
6. Name, address, and signature of proposer member of the Division of Rubber Chemistry.....

FIELDS NOT YET FULLY RECOGNIZED

Among fields which have not been fully recognized may be mentioned: Physics of rubber, including kinetic theory, dynamic and electrical properties; reinforcement; oxidation; antioxidants; polysulfide rubbers (Thiokol); polychloroprene (Neoprene); vulcanizable copolymers of isobutylene and dienes (Butyl); cold GR-S and oil-extended GR-S; polyacrylate rubbers; silicone rubbers; isocyanate rubbers; reclaiming; physical testing; delayed-action accelerators; new reinforcing fillers; new processing equipment.

CHARLES GOODYEAR MEDALISTS

- 1941 DAVID SPENCE. A pioneer of rubber chemistry, who did much important early work. No lecture given.
- 1942 L. B. SEBRELL. Research on antioxidants and accelerators. Lecture: "The Second Mile", *Industrial and Engineering Chemistry*, 1943, p. 736; *RUBBER CHEMISTRY AND TECHNOLOGY*, 1943, p. 713.
- 1944 W. L. SEMON. Synthetic rubber research. Lecture: "Research leading to commercial butadiene synthetic rubber", *Chemical and Engineering News*, 1946, p. 2900; *India Rubber World*, December 1956.
- 1946 IRA WILLIAMS. Neoprene and overall accomplishments. Lecture: "Vulcanization of rubber with sulfur", *Industrial and Engineering Chemistry*, 1947, p. 901.
- 1948 GEORGE OENSLAGER. Pioneer in organic accelerators. No lecture given.
- 1949 H. L. FISHER. Long in the field of rubber chemistry; over all accomplishments. Lecture: "Rubber research and the need for a rubber research institute in the United States".
- 1950 C. C. DAVIS. Development of the oxygen bomb test for accelerated aging; *Chemical Abstracts*; *RUBBER CHEMISTRY AND TECHNOLOGY*; Editor "The Chemistry and Technology of Rubber". Lecture: "Some of the real pioneers of the rubber industry", *India Rubber World*, 1951, p. 433.
- 1951 W. C. GEER. Oven aging test, de-icer for airplanes, encouragement of rubber research. Lecture: "Strategy in rubber research". *Industrial and Engineering Chemistry*, 1951, p. 2436.
- 1952 H. E. SIMMONS. One of the early and best known teachers of rubber chemistry, and an inspirational guidance of younger men. Lecture: "Out of the past".
- 1953 J. T. BLAKE. Research on oxidation and vulcanization. Co-editor of "The Chemistry and Technology of Rubber". Accumulative accomplishments. Lecture: "The future of rubber". *Chemical and Engineering News*, 1953, p. 4290.
- 1954 G. S. WHITBY. Research on plantation rubber, vulcanization, accelerators, GR-S synthesis, overall accomplishments. Editor of "Synthetic Rubber". Lecture: "Reflections on rubber research". *Industrial and Engineering Chemistry*, 1955, p. 806.
- 1955 R. P. DINSMORE. Numerous important contributions to rubber chemistry and technology; recipient of honors. Lecture: "Specifications for a rubber chemist".

GORDON RESEARCH CONFERENCES, AAAS

The Gordon Research Conferences of the American Association for the Advancement of Science for 1956 will be held from June 11 to August 31 at Colby Junior College, New London, New Hampshire, New Hampton School, New Hampton, New Hampshire, and Kimball Union Academy, Meriden, New Hampshire.

The Conferences were established to stimulate research in universities, research foundations, and industrial laboratories. This is a valuable means of disseminating information and ideas which otherwise would not be realized through normal channels of publication and scientific meetings. In addition, scientists in related fields become acquainted, and valuable associations are formed which result in collaboration and cooperative effort between different laboratories.

The purpose of the program is not to review the known fields of chemistry, but primarily to bring experts up to date as to the latest developments, analyze the significance of these developments, and promote suggestions as to underlying theories and profitable methods of approach for making new progress. This purpose is achieved by an informal type of meeting consisting of scheduled lectures and free discussion groups.

Requests for attendance at the Conferences, or for any additional information should be addressed to W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From June 11 to August 31, 1956, mail should be addressed to Colby Junior College, New London, New Hampshire.

The conference on ELASTOMERS will be held at Colby Junior College, New London, New Hampshire, July 30-August 3.

The following papers are scheduled for presentation:

July 30

- S. N. MUCHNICK. Adhesive Bonding of Metals.
- D. M. ALSTADT. Fundamentals of Rubber Adhesion.
- S. M. OHLBERG and L. E. ALEXANDER. Crystallinity and Orientation in Organosiloxane Polymers—x-Ray Diffraction Studies.
- E. L. WARRICK. Crystallinity and Orientation in Organosiloxane Polymers—Physical Measurements.

July 31

- G. NATTA. Synthesis by Anionic Polymerization of New Elastomers and Unsaturated Crystalline Polymers.
- General Discussion of Synthesis and Properties of *Cis*-Polyisoprene and Related Polymers.
- W. S. McNATT. Biosynthesis of Rubber.

August 1

- R. M. PIERSON. Formation and Properties of Networks Involving Addition Polymers Having Reactive End Groups.
- H. WESTLINNING. Interaction Between Rubbers and Fillers.
- G. KRAUS. The Significance of Swelling Equilibria in Carbon Black Reinforced Elastomers.

August 2

- J. W. SELLERS, D. INMAN, and M. P. WAGNER. Reinforcement by Fine Particle Silica.
- I. AUERBACH, W. C. KURTYLA, and S. D. GEHMAN. A Diffusivity Approach for Studying the Molecular Structure of Elastomers.
- L. MULLINS. Recent Developments in Theories of Elastic Behavior and Mechanical Failure of Rubber.

August 3

- K. W. SCOTT. Dynamic Properties of Strained Elastomers.
- J. P. BERRY. Stress Relaxation of Natural Rubber Vulcanizates.

FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY, PHILADELPHIA, PA., NOVEMBER 2-4, 1955

The 68th Meeting of the Division of Rubber Chemistry was held in Philadelphia, November 2-4, 1955, with headquarters at the Bellevue-Stratford Hotel. The Meeting was attended by 1,370 members and guests, which represented the largest attendance that we have ever had at one of our meetings.

The 25-Year Club met under the Chairmanship of Arthur Nellen, with approximately 200 present. The contest for the longest service in the rubber industry was won by H. B. Underwood of Minnesota Mining and Manufacturing.

The banquet was attended by approximately 750 members and guests. The highlight of the banquet was the presentation of the Goodyear Medal and Scroll to R. P. Dinsmoore of Goodyear Tire and Rubber Company.

The Executive Committee appointed H. I. Cramer as Councillor for the Rubber Division for the term 1956-59, and John Ball as the Alternate Councillor for the same term.

The Executive Committee also authorized the appointment of an Associate Editor for *Rubber Chemistry and Technology*.

At the Business Meeting, recognition was made of the deaths since the last meeting of C. Brobiel, N. C. Hill, C. H. Masland, 2nd, G. Egloff, and G. S. Haslam.

Changes in the By-Laws of the Division were also ratified by the membership. The new By-Laws provided the following three services for the Division:

1. The establishment of a Director representing the membership resident in Canada.
2. A revision of the fiscal year of the Division.
3. The establishment of two Library Committees.

The officers for 1956, who had been elected by mail ballot, were announced.

The following papers were presented:

Ozone Cracking of Rubber: Objective Evaluation through Creep Measurement.

H. M. LEEPER AND G. L. GABLE (Monsanto Chemical Co., Nitro, West Va.).

Exposure Tests of Chlorosulfonated Polyethylene Compounds. H. A.

WINKELMANN (Dryden Rubber Division, Sheller Manufacturing Corp., Chicago, Ill.).

A Study of the Effects of Gamma Radiation on Rubber Compounds and Polymers. J. W. BORN (B. F. Goodrich Research Center, Brecksville, Ohio).

The Technical Manpower Situation. A. W. DAVISON (Engineering Manpower Commission, Engineers Joint Council, New York, N. Y.).

The Effect of High Temperature on the Properties of Organic and Silicone Rubbers. G. M. KONKLE, J. T. MCINTYRE, AND J. V. FENNER (Dow-Corning Corp., Midland, Mich.).

Compounding of Silicone Rubber. IV. Testing of Silicone Rubber at Elevated Temperatures. ALDO J. DE FRANCESCO, ROGER D. ALLING, AND JOHN H. BALDRIDGE (Connecticut Hard Rubber Co., New Haven, Conn.).

A Discussion of Some Factors Influencing the Duplicability of Tire Road Wear Testing. L. R. SPERBERG (Three-T-Fleet, Odessa, Texas).

- Highly Stabilized Non-Discoloring Rubber Compositions. D. B. MERRIFIELD (Monsanto Chemical Co., Nitro, West Va.).
- Vulcanization of Butyl with Other Rubbers. F. P. FORD AND R. L. ZAPP (Esso Research and Engineering Co., Linden, N. J.).
- Sulfur Vulcanization of Vinyl-Substituted Polysiloxanes. K. E. POLAMANTEER AND R. J. KOCH (Dow-Corning Corp., Midland, Mich.).
- Effect of Varying the Vulcanization Temperature on the Physical Properties Of Black-Reinforced Tread Compounds. J. V. SVETLIK AND H. E. RAILSBACK (Phillips Petroleum Co., Bartlesville, Okla.).
- The Effect of Carbon Black on the Oxidation of Rubber. F. LYON, K. A. BURGESS, AND C. W. SWEITZER (Columbian Carbon Co., New York, N. Y.).
- Goodyear Medal Lecture: Specifications of a Rubber Chemist. R. P. DINSMORE (Goodyear Tire and Rubber Co., Akron, Ohio).
- Carboxylic Rubber. J. GREEN AND E. F. SVERDRUP (U. S. Rubber Reclaiming Co., Buffalo, N. Y.).
- Ameripol SN—A Synthetic Cis-Polyisoprene. I. Polymer Preparation and Properties. S. L. HORNE, JR., J. P. KIEHL, J. J. SHIPMAN, AND V. L. FOLT (B. F. Goodrich Co. Research Center, Brecksville, Ohio).
- Ameripol SN—A Synthetic Cis-Polyisoprene. II. Processing and Vulcanization. E. A. WILLSON (B. F. Goodrich Co. Research Center, Brecksville, Ohio).
- Ameripol SN—A Synthetic Cis-Polyisoprene. III. Tire Testing. M. A. REINHART AND E. A. WILLSON (B. F. Goodrich Research Center, Brecksville, Ohio).
- A Cis-Polyisoprene Having the Molecular Structural Features of Hevea Rubber. F. W. STAVELY (Firestone Tire & Rubber Co., Akron, Ohio).
- Kel-F Elastomer: Properties and Applications. M. E. CONROY, F. J. HONN, L. E. ROBB, AND D. R. WOLF (M. W. Kellogg Co., Jersey City, N. J.).
- Polyacrylic Ether-Ester Elastomers. I. The Compounding and Properties of Vyram Polyacrylic Elastomer. C. L. GABLE, H. W. KILBOURNE, P. E. MCINTYRE, AND M. J. PUGH (Monsanto Chemical Co., Nitro, West Va.).
- Control of Polymer Breakdown in Oil-Polymer Masterbatches. W. K. TAFT, J. DUKE, T. B. LARCHAR, SR., W. G. KITZMILLER, AND M. FELDON (Government Laboratories, University of Akron, Akron, Ohio).
- Correlation of Polymer Breakdown with Absorbency Index. W. K. TAFT, J. DUKE, D. PREM, AND A. D. SNYDER (Government Laboratories, University of Akron, Akron, Ohio).
- A Glass Polymerization Vessel for Small-Scale Laboratory Studies. J. D. SUTHERLAND AND J. P. MCKENZIE (Copolymer Rubber & Chemical Corp., Baton Rouge, La.).
- Thermal Degradation of Vulcanized and Unvulcanized Rubber in a Vacuum. S. STRAUS AND S. L. MADORSKY (National Bureau of Standards, Washington, D. C.).
- Determination of Degree of Cure in Filler-Reinforced Vulcanizates by the Swelling Method. GERALD KRAUS (Phillips Petroleum Co., Bartlesville, Okla.).
- Mixing Studies of Zinc Oxide in a Banbury. H. O. JONES AND E. G. SNYDER (New Jersey Zinc Co., of Pa., Palmerton, Penna.).

REVUE GÉNÉRALE DU CAOUTCHOUC

The many readers of the French rubber journal, *Revue Générale du Caoutchouc*, have doubtless been pleased to witness the growth and development of this interesting and valuable journal since its beginning many years ago.

The journal has now acquired a "new look," with its larger size and increased amount of valuable information pertaining to science, technology, and industry. Particular attention is called to the publication of technical papers in English. Heretofore rubber chemists and technologists have been obliged to await the later appearance of many papers in RUBBER CHEMISTRY AND TECHNOLOGY, but now papers are appearing in English in the French journal.

With these papers in English, and with excellent abstracts of the journal and patent literature, an increasing number of rubber chemists and technologists, organizations, and libraries should find it highly desirable to subscribe to the *Revue Générale du Caoutchouc* for the interesting and valuable information which it publishes.

NEW BOOKS AND OTHER PUBLICATIONS

PRACTICAL LATEX WORK. By H. J. Stern. Published by the Blackfriars Press, Ltd., Smith-Dorrien Road, Leicester, England. $4\frac{1}{2} \times 7\frac{1}{2}$ in. 96 pp. (Tentative price \$2.00).—This is the third edition of the book, originally published in 1940. Since publication of the second edition, two important changes have occurred. In the first place, many patents have now expired, so that processes previously confined to one concern are now available to all. Foam is the most important example in this category. Second, a wide range of synthetic latex is now available. Both these factors have made it necessary for the author to include much new material. Apart from the section on spreading, little has been omitted from this new edition.

In rewriting the greater part of the text, Dr. Stern has made a new presentation of much of the subject matter, with emphasis on those applications of greatest importance in the industry. Those sections dealing with latex foam, thread, paper, and rubberized hair have been expanded. The chapter on synthetic latexes has been greatly enlarged and should be of considerable value to those interested in evaluating these new materials in both new and old operations. In presenting this new edition, the author has held to his original objective to supply the type of information required in daily operations.

In this work, Dr. Stern presents a discussion of natural latex; the preparation of mixes for rubber manufacture; the manufacture of dipped goods; synthetic latexes and their applications, and miscellaneous processes, including the application of latex to textiles and fibers. He also discusses the cost factor as it applies to latex work. The book offers many interesting photographs, diagrams and tabular material. A complete table of contents has been provided. [From the *Rubber Age* of New York.]

FUTURE TRENDS IN CARBON BLACKS. By I. Drogin. United Carbon Co., Inc., Charleston, W. Va., $4\frac{1}{2} \times 8\frac{1}{2}$ in. 16 pp.—This publication is a reprint of a paper given by Dr. Drogin before the Swedish Institution of Rubber Technology held in Stockholm, November 26-27, 1954. The paper reviews briefly the progress made in the past for modernizing carbon black, its present status, the superabrasion furnace types of black already being used for increasing the mileage of tire treads and improving their resistance to cracking, and the types of blacks required for the technically classified natural rubbers, the new types of synthetic rubbers, cold rubber, and rubbers extended with large quantities of oil. Consideration is also given to the types of blacks required to give satisfactory performance of tubeless tires and of the tires used on the newer passenger cars and trucks equipped with more powerful engines. The future trends in carbon black, according to the paper, point to fewer types. In the author's opinion, it is possible to reduce the number of types of blacks in general use now to three types, as follows: (1) A carbon black for tire treads, (2) A general purpose carbon black for tire carcasses and sidewalls and for higher quality mechanical goods, (3) A low cost black primarily for mechanical goods. [From the *Rubber Age* of New York.]

BUNA, HERSTELLUNG, PRÜFUNG, EIGENSCHAFTEN. W. Breuers and H. Luttrupp. Published by VEB Verlag Technik, Berlin. 1954. Cloth, 7 by $9\frac{1}{2}$ inches, 427 pages, illustrated.—Although Germany pioneered the actual production and use of synthetic rubber, particularly the Buna types, very little literature in book form has hitherto appeared on the subject in the German language. The present work is an attempt by the authors, both active at the Schkopau Buna works in East Germany, to fill this lack, and in this aim they

have largely succeeded. Each of the three main parts of the book, headed, respectively, "Production and Properties of Unprocessed Buna", "Testing Methods for Buna", and "Compounds and Vulcanizates", discusses in numerous sections practically every aspect of the subjects indicated by these titles.

In Part I a brief history of the development of Buna is followed by a systematic treatment of production—from the monomers, through polymerization methods and the manufacture of the various types of Bunas and Perbunans in Germany, as well as of the GR-S rubber in America—and the properties of Buna.

In Part II—the longest and most complete section—practically every kind of chemical and physical testing method used in Germany and America for Buna-type rubbers (with a few Russian and British tests added for good measure) finds a place, accompanied by numerous graphs, tables, and illustrations of apparatus and test results on samples.

The third and last part of this book covers the action of various compounding ingredients, processing and—in greater detail—fillers and the comparative properties of different natural rubber and Buna compounds, as well as the results obtained by mixing Buna S3, S4, and S5 with natural rubber. Various German carbon blacks and one Rumanian black are described, and the effect of increasing amounts added to Buna are shown in several graphs and tables; other tables show how these blacks compare with Philblack O, and still another series indicates the action of white fillers.

The book is fully documented—every sub-section closes with a list of references, some of hitherto unpublished material; many patents are also mentioned. Good indexes of authors and subjects conclude a book that should prove a valuable source work for all interested in Buna synthetic rubbers. [From the *Rubber World*.]

HEEL AND SOLE COMPOUNDING. By C. W. Lawson. Naugatuck Chemical Division, U. S. Rubber Co., Naugatuck, Conn. $8\frac{1}{2} \times 11$ in. 32 pp.—This bulletin describes the manufacture of heels and soles. Photographs depict milling, cutting, and molding of the raw stock as well as trimming and inspection of the finished product. Particular attention has been paid to economy in cost and good processing characteristics. Some 40 compounds are shown, including those utilizing GR-S 1503 and 1013 and blends of GR-S and natural rubber. Data on tear resistance, abrasion index, permanent set, elongation, tensile and 200 per cent modulus are given on press cures of 3, 6, 8 and 10 minute cycles. In addition, the formulations are arranged according to high quality types, standard quality, competitive quality, Army grade, and super quality. [From the *Rubber Age* of New York.]

INTERNATIONAL RUBBER DIRECTORY. Second Edition. Publishers, Verlag fuer Internationale Wirtschaftsliteratur GmbH., P.O.B. 108, Zurich 47, Switzerland. Cloth, 6 by 9 inches, 576 pages. Price, \$12.80.—This is the second edition of the Swiss trilingual (English, French, German) directory of the world's rubber goods manufacturers, and it mirrors the continuing expansion of the industry since the first edition was published in 1953. That volume had 150 pages less than the current compilation, and considering that this 1955 edition was based on data compiled during 1954, it seems certain that the third edition yet to be published, based as it will be on this boom year 1955, will be larger still. The United States, for example, had 45 pages of rubber manufacturers listed in the first edition, with 60 pages now devoted to it in the present volume. Other countries reflect a similar growth.

Again, in addition to the main listings of firms, the number of their employees, and the sort of goods they manufacture, there are sections devoted to associations and federations, schools and research laboratories, periodicals, a comprehensive buyers' guide, a complete alphabetical manufacturers index, and a trilingual technical vocabulary to aid the international sale and purchase of products. [From the *Rubber World*.]

THE SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS. By Ralph L. Shriner, Reynold C. Fuson, and David Y. Curtin. Fourth Edition, 1956. Published by John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y. 426 pp. \$6.00. In this new edition, the latest theories and techniques are included to modernize a volume which has already enjoyed twenty years of practical service. The book again provides reliable procedures for the preparation of numerous useful derivatives of organic compounds, and up-to-date discussions of the most important types of organic reactions. The authors have added a new chapter on infrared and ultraviolet spectroscopy, giving full indications for their use with the common functional groups. The discussion of reaction mechanisms has been revised, and new theories are employed in the subjects of relative reactivities, physical properties, and solubility behavior.

The chapters include the identification of unknowns, preliminary examination, determination of physical properties, qualitative analysis for the elements, solubility classes, application of classification tests, use of spectroscopic methods for functional group determination, preparation of derivatives, tables of derivatives, separation of mixtures, and the solution of structural problems.

CHEMICAL TRADE NAMES AND COMMERCIAL SYNONYMS. Second Edition. By Williams Haynes. Published by D. Van Nostrand Co., 120 Alexander St., Princeton, N. J. 6 × 9 in. 480 pp. \$8.00.—Containing over one-quarter more entries than its predecessor, this revised edition gives precise and complete definitions of the special names used in the modern chemical industry. It covers both abbreviations adopted to simplify long technical names of the newer organic compounds and those terms coined by manufacturers. The terms listed in this book are confined to chemicals and chemical specialties sold in the industrial field. It includes specialties used in the rubber, paint, varnish, textile, metallurgical, and other industries. Definitions comprise generally two parts: first, the composition, and second, the chief uses. The uses recorded are indicative rather than inclusive. The uses of many items are literally legion, and in many cases the applications are exceedingly specialized, so users are urged to write the manufacturers direct—hence the index with their addresses—for detailed information. [From the *Rubber Age* of New York.]

ASTM STANDARDS ON PLASTICS. Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 × 9 in. 812 pp. \$5.75.—This compilation presents in convenient form ASTM standards and tentative specifications, methods of physical testing, recommended practices, methods of analysis, and definitions of terms pertaining to plastics. It has been substantially revised since the previous edition was published in May 1954. Of the total of 143 specifications and tests, four are entirely new and 41 have been either revised, reaffirmed, or advanced from tentative status to standard. Two others have been discontinued, one has been replaced, and another has been redesignated as a general method applicable to materials other than plastics. The standards in the book have been developed by ASTM Committee D-20 on Plastics and will be of special value to plastics engineers and to those concerned with the design and production of plastics and items in which plastics are used.

In addition to the standards prepared by Committee D-20, there have been included a number of specifications, methods of testing, recommended practices, and definitions applying to plastics in the electrical insulation field which are under the jurisdiction of Committee D-9 on Electrical Insulating Materials. Other standards of interest in the testing of plastics and developed by other Society committees are included. [From the *Rubber Age* of New York.]

CHEMICAL ENGINEERING CATALOG. 1955-56. Reinhold Publishing Corp., New York, N. Y. Cloth, 8½ by 11¼ inches, 1917 pages. Price, \$12.50.—This fortieth annual edition of the catalog contains, as in the past, photographs, descriptions, and specifications of industrial equipment available through American manufacturers or dealers. The volume is sectionalized into six indexes: company name, function of equipment, equipment and materials of construction, plants and specialized services, pilot-plant manufacturers, and trade names. More than 550 equipment manufacturers and their products are contained in this latest compilation. [From the *Rubber World*.]

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STUDIES OF THE VULCANIZATION OF HIGH ELASTIC POLYMERS.* I. THE VULCANIZATION OF NATURAL RUBBER WITH THIURAM DISULFIDES

PART 1

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INTRODUCTION

Perhaps nowhere in chemistry is there encountered a field which even in its literature alone shows so many uncertainties and (possibly only apparent) contradictions as that of the vulcanization of rubber. This is especially felt when one attempts to develop a clear-cut picture of the state of affairs based on the numerous individual observations as well as on the theoretical concepts that have been developed. In view of these conditions, which, moreover, entail in practical circles a discussion devoid of scientific basis, it was decided to carry out an experimental study with the goal of collecting our own experiences and thereby, in each particular topic, to contribute to clearing up the situation.

The overemphasis and, as it sometimes seems, the overvaluation of physical (technological) criteria in the investigations of vulcanization may have contributed to the failure to attach to purely chemical investigation in this field the importance that it actually deserves. This may explain the fact that analytical studies arouse even less interest than they should. Yet it will never be possible to obtain essential insight into the processes taking place in vulcanization unless both physical and chemical studies are carried out simultaneously, and unless, in carrying out the latter, the analytical bases which are prerequisites for the task are created or further developed.

The reason for prefacing these remarks is that the results presented in this paper on the vulcanization of rubber with thiuram disulfide could not have been accomplished without the application of methods of analysis developed by us.

Investigations aimed at explaining the vulcanization of rubber with thiuram disulfide should arouse the interest of both the practical rubber technologist and the scientist. This is because thiuram disulfides are themselves vulcanization agents and yet, in the presence of sulfur, act like other vulcanization accelerators.

In the literature one finds numerous publications which deal with the vulcanization of rubber with thiuram disulfide. None of them, however, appears able to answer exhaustively the question of the reaction that takes place. Bruni and Romani¹ have put forward the view that tetramethylthiuram disulfide, the most commonly, if the only thiuram disulfide studied, is broken up at the temperature of vulcanization into sulfur and its monosulfide. They con-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi*; Part I from Vol. 7, No. 12, pages WT 273-279, December 1954; Part II from Vol. 8, No. 1, pages WT 2-8, January 1955; Part III from Vol. 8, No. 2, pages WT 27-31, February 1955; Part IV from Vol. 8, No. 4, pages WT 85-90, April 1955, and Part V from Vol. 8, No. 10, pages WT 251-257, October 1955. Part I is based on a lecture given at the meeting of the Deutsche Kautschuk-Gesellschaft in Munich, October 21-23, 1954.

sider that the sulfur released, which is surely highly active, effects the crosslinking by sulfur bridges of the macromolecules. Bedford and his coworkers² also explained the vulcanization with tetramethylthiuram disulfide in this way. Finally in this connection one is reminded of the thermal splitting at higher temperatures of tetramethylthiuram disulfide into sulfur, carbon disulfide, and tetramethylthiourea³. This can be regarded as a thermal decomposition of the disulfide in which the thiuram monosulfide is an intermediate product. Here too the actual vulcanizing agent is sulfur; yet the course of this process would produce a different situation, inasmuch as it precludes the formation of tetramethylthiuram monosulfide. But we know that this particular compound, although itself not a vulcanizing agent, is capable of accelerating the vulcanization of rubber by sulfur. To explain this, the formation of thiuram disulfide and even of its higher sulfides is assumed. These are supposed to transfer sulfur to the rubber and form thiuram monosulfide again. If this course of the reactions in question is assumed, then vulcanization can take place only if equilibrium prevails between the partners (sulfur, thiuram monosulfide, thiuram polysulfide (?)). This view is in accord with the conclusions drawn from their investigations by Craig and coworkers⁴. Yet we do not know of any experimental proofs that actually demonstrate the occurrence of such equilibria.

If the above reactions occur at all in the vulcanization with tetramethylthiuram disulfide, they are not in any case the only ones. This can be seen from the work of Cummings and Simmons⁵, Shepard⁶, and Shimmada⁷, in which the formation of zinc dimethyldithiocarbamate is noted in the vulcanization of rubber with tetramethylthiuram disulfide in the presence of zinc oxide. (Demonstration of the presence of dithiocarbamate by its characteristically colored heavy-metal salts). The formation of zinc dithiocarbamate in thiuram vulcanization has since been abundantly established, among others by Stiehler and Wakelin⁸ in an x-ray study. The proof of the presence of dithiocarbamate in the extracts of thiuram vulcanizates naturally opens the way to new points of view. The formation of this compound may be attributed to a reduction of the thiuram disulfide, in which the rubber furnishes the necessary hydrogen. The chain radicals which result could then mutually satisfy each other and thus lead to cross-linking by C—C bonds. A cross-linking by C—C bonds is discussed by Gee⁹ and by Farmer and Michael¹⁰, and these authors attribute to the thiuram disulfide a reaction mechanism analogous to that of benzoyl peroxide. Similar considerations are entertained by Bloomfield¹¹. To be sure, Farmer appears nevertheless to believe that there is a splitting off of the sulfur from the disulfide¹².

Of all the publications which concern themselves with thiuram vulcanization, we have found the investigation of Jarrijo¹³ to be of special interest, although in the literature in general it has received only slight mention. The work of Jarrijo, in which the presence of zinc dimethyldithiocarbamate is shown by spectroscopic methods and the conversion of the thiuram disulfide to dithiocarbamate is studied quantitatively, leads to the result that always 70–76 per cent of the thiuram disulfide goes over into dithiocarbamate, and while the vulcanizates contain sulfur, no thiuram monosulfide can be found. From this, Jarrijo concludes that thiuram vulcanization depends exclusively on formation of C—C bonds, brought about by dehydrogenation of the rubber by thiuram disulfide. He postulates that the disulfide, with its $=N-C(S)-S$ groups, attaches to the double bonds and that the addition product reacts with the structural units of the rubber macromolecules, liberating dithiocarbamic acid and regenerating C—C bonds. This interpretation of his results, although

plausible in itself, is not sufficient to explain the consistent 70-76 per cent conversion.

Jarrijon is not in accord with the previously discussed concepts of thiuram vulcanization, since his conclusions categorically exclude the contribution of sulfur to the vulcanization. His view prompts us to compare thiuram disulfide as a vulcanizing agent with other compounds, such as quinonedioximes and their derivatives¹⁴, aromatic dinitro compounds¹⁵, diazoamino compounds¹⁶, which are likewise able to vulcanize rubber and concerning which Ostromislensky¹⁷ has postulated that they react with rubber in a sort of oxidation-reduction reaction.

The above comments clearly bring out the variance between the views that prevail concerning the mechanism of thiuram vulcanization, and emphasize the need of a new and more fundamental treatment. We have considered it desirable to follow the material conversion quantitatively as a function of both the reaction time and the temperature, and at the same time to use homologous thiuram disulfides in order to study the influence of their particular chemical constitution. All the investigations were carried out with natural rubber and with zinc oxide present, which we regard only as a basic raw material. The vulcanizing agents were tetramethyl-, tetraethyl-, and tetrapropylthiuram disulfide. They were prepared in the conventional manner from the corresponding secondary amines and carbon disulfide by oxidation of initially formed salts of dithiocarbamic acid with hydrogen peroxide or iodine.

EXPERIMENTAL

PREPARATION OF THE VULCANIZATES

All vulcanizates were prepared with natural rubber (pale crepe) after 72 hours' acetone extraction in the Soxhlet apparatus. Breakdown on the rubber mill was kept as slight as possible by keeping the rolls at 60-70° C. As soon as the stock formed a fairly smooth layer on the rolls, the zinc oxide was first added and then the particular thiuram disulfide. Special care was taken when the thiuram disulfide was added to hold the roll temperature as low as possible (about 50° C). This was to preclude any appreciable effect on the result of reactions that might be initiated even at lower temperatures. The prepared mixes did not emit the slightest odor other than that of masticated rubber.

Vulcanization was carried out at different temperatures and the reaction time varied systematically. The experiments were, moreover, conducted in a thermostat (with paraffin oil as medium). The samples were contained in closed molds. At the end of the vulcanization period they were quickly cooled in order to stop the reaction. This is especially important when the reaction time is short. It is interesting to note that, even when the molds were opened, no odor of any sort such as carbon disulfide, amine, etc., was perceived, which would have suggested occurrence of thermal splitting.

All the batches contained an excess of zinc oxide, namely, about five times the amount necessary for combination with the dithiocarbamic acid that would eventually be evolved from the added thiuram disulfide. The thiuram concentration in the rubber was generally 0.1 to 0.2 millimole per gram, i.e., very much less than that corresponding to the number of double bonds.

We did not undertake to determine the physical (technological) characteristics, e.g., the modulus, since, apart from the fact that the physical properties of the vulcanizates depend on the degree of breakdown, which we do not characterize in any case, they naturally vary with the amount of the added thiuram

disulfide. This has been studied more closely by Morrison and Shepard¹⁸. We were interested in the mechanism of the vulcanization reaction itself, and this is a chemical problem.

THE ANALYSIS OF VULCANIZATES

For analysis, the vulcanizates were cut into small pieces and extracted in the Soxhlet apparatus either with acetone (practically no swelling), or with cyclohexane (considerable swelling). The extraction was found by careful tests to be quantitative after 48 hours with acetone and after 24 hours with cyclohexane, as shown by the absence of a red coloration on the addition of copper sulfate to the extract after concentration by evaporation.

The extracts were analyzed quantitatively by the conductometric methods developed by us¹⁹. These proved to be very reliable. It is necessary, however, to make a few remarks about the behavior of the zinc dialkyldithiocarbamates and the tetraalkylthiuram disulfides, as well as their binary solutions in boiling organic solvents, before we describe briefly the course of the analysis.

When solutions of zinc dimethyl-, zinc diethyl-, or zinc dipropyldithiocarbamate in acetone or cyclohexane are heated to boiling for 24 hours or even longer, these compounds do not undergo any change at all. This is shown by the fact that, after evaporation of the solutions to dryness in vacuo and again dissolving the residue in acetone, one obtains by conductometric titration with hydrochloric acid the same amount of added dithiocarbamate within the limits of accuracy of the titration method. Under the same conditions, thiuram disulfides behave quite differently. They undergo evident decomposition, which occurs most rapidly in the case of tetramethylthiuram disulfide, appreciably slower with tetraethylthiuram disulfide, and with tetrapropylthiuram disulfide is practically no longer observed provided its solutions are not kept boiling for excessive lengths of time. A definite dependence of decomposition velocity on the type of solvent can be noted. All three thiuram disulfides are much more stable in cyclohexane than in acetone, so that tetrapropylthiuram disulfide can apparently be treated with boiling cyclohexane indefinitely without appreciable decomposition. Even tetraethylthiuram disulfide shows but slight breaking down after boiling in this solvent for 24 hours. Tetramethylthiuram disulfide, however, suffers considerable decomposition. The above described relationships can be derived from the quantitative analysis of the solutions. To this end the particular solvent is distilled in vacuum, the residue taken up in acetone, and diluted with water. This solution is then titrated conductometrically with copper sulfate in the presence of hydroquinone. We have not made any detailed study of the nature of the decomposition.

A noteworthy fact that is important in the analysis of vulcanizates is that the splitting up which thiuram disulfides undergo occurs much more rapidly if zinc dialkyldithiocarbamate is present. The influence of the zinc dithiocarbamate on the process is again most marked with tetramethylthiuram disulfide and is most in evidence in acetone solutions, whereas cyclohexane solutions of thiuram disulfide and zinc dithiocarbamate are much more stable. Even tetrapropylthiuram disulfide, which we have stated to be quite stable, undergoes appreciable although relatively slight decomposition in the presence of zinc dipropyldithiocarbamate. In all cases, however, the particular zinc dialkyldithiocarbamate remains unchanged. These observations can be followed quantitatively if the solutions are treated as described above and then the water-acetone solution is first titrated with hydrochloric acid to determine the dithiocarba-

mate and then, after the greater part of the acid has been neutralized, titrated with copper sulfate in the presence of hydroquinone to determine the thiuram disulfide. An alternative method is to treat the solution with dodecanethiol, which reduces the thiuram disulfide to the dialkylammoniumdithiocarbamate, with splitting off of carbon disulfide, and then to determine the sum of the thiuram disulfide and dithiocarbamate by conductometric titration with acid. The dithiocarbamate is determined in a separate sample of the solution, which does not require any special treatment. This also is done by means of conductometric titration with acid. From the difference between the two analytical results, the amount of the thiuram disulfide can be calculated. This indirect method of course gives exact results only if both compounds are in fairly comparable molar concentrations.

These observations concerning the instability of the thiuram disulfides in organic solvents must be considered in making quantitative analyses of vulcanizates, for it is a primary problem to determine with the greatest possible accuracy the change in the thiuram disulfide concentration with time of vulcanization.

When the above considerations are kept in mind, the quantitative analysis of the zinc dithiocarbamate in vulcanizates is relatively simple. The procedure was as follows. In order to prevent interference of the acidimetric conductometric titration of the dithiocarbamate, etc., by decomposition products of residual unconverted thiuram disulfide (amine), the extracts were first dried in vacuum. The evaporated solids were taken up in acetone and diluted to a known volume in a measuring flask. Aliquot parts of this solution were introduced into the conductivity cell and diluted with water in such amount that precipitation of the dissolved compounds was avoided. Then they were titrated with hydrochloric acid of known concentration. The conductivity cell was kept at 40° C in a thermostat. Care was taken to see that the galvanometer deflections were constant after each addition of the acid. This is because the acid splitting of the dithiocarbamates proceeds with measurable velocity, most slowly in the case of zinc dipropyldithiocarbamate. At least two titrations were made on each extract. When the analyses were carefully carried out, the results agreed within the limits of error of the method. The titration curves were consistently faultless when all necessary measures were taken. Small quantities of rubber components carried on into the extract evidently have no appreciable effect on them.

That the acidimetric conductometric titration of the dithiocarbamate is not disturbed by the presence of thiuram disulfide has been shown by us¹². In order to be completely sure about this, however, in some experimental runs we have determined the zinc at the same time by potentiometric titration with sodium hydroxide, after breaking down the dithiocarbamate with acid. Both potentiometric and conductometric titration generally proved to give good agreement between the calculated dithiocarbamate and that found, but the zinc determination, especially in vulcanizates having short reaction times, gives slightly too high values. Nevertheless, there are practically no discrepancies between the results of the two analyses provided the vulcanizates have been sufficiently thoroughly cured. The slightly too high dithiocarbamate analyses which are occasionally obtained with not sufficiently cured vulcanizates in the alkalimetric potentiometry of zinc can be explained by the tendency of the thiuram disulfide to decompose in the presence of bases when the analyses are made on vulcanizates having short reaction times. (See below). In this case more sodium hydroxide is consumed than corresponds to the zinc present.

Such discrepancies are naturally not observed in thoroughly cured vulcanizates, since these contain practically no residual thiuram disulfide. We may, therefore, conclude that the conductometric titration of the extracts is capable of giving exactly within the limits of error of the method the amount of zinc dithiocarbamate formed during the vulcanization.

The quantitative determination of the thiuram disulfide proves to be somewhat more complicated. It is, to be sure, quite possible, after destroying the dithiocarbamate with acid, to determine the thiuram disulfide in the same solution by conductometric titration with copper sulfate. Such analyses, however, no matter how carefully they are conducted, are bound to give false results because, under the conditions of the extraction, the thiuram disulfides will have become partially decomposed.

We have convinced ourselves that the decomposition suffered by tetraethyl- and tetrapropyldithiuram disulfide during extraction can be prevented by extracting with boiling cyclohexane over a layer of dilute hydrochloric acid.

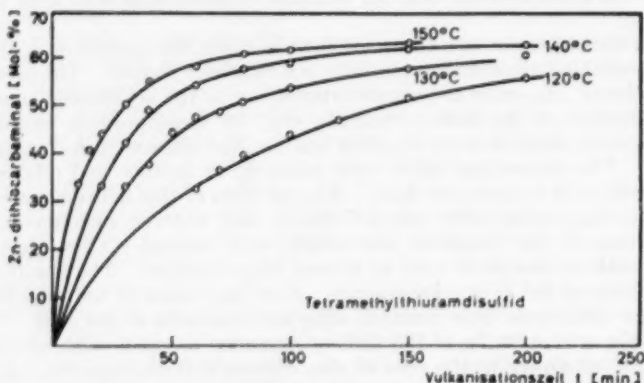


FIG. 1.—Increase of zinc dithiocarbamate (in mole-per cent of the added thiuram disulfide) with time of vulcanization with tetramethylthiuram disulfide (extraction with boiling acetone).

Any dithiocarbamate that is dissolved by the cyclohexane is immediately decomposed under these conditions. Zinc chloride as well as the corresponding dialkylammonium chloride which form in the acid splitting of the dithiocarbamate are taken up by the aqueous layer, whereas the thiuram disulfide remains in the cyclohexane. At the end of the extraction, the two strata are separated in a separatory funnel and the cyclohexane solution is prepared for analysis in the manner already described. The determination of the thiuram disulfide can then be carried out by conductometric titration with copper sulfate in the presence of hydroquinone or alternatively by the thiol method.

EXPERIMENTAL RESULTS AND DISCUSSION

For the sake of saving space, it is not expedient to include the whole body of experimental material in tabular form. This would hardly be worthwhile, for it can be shown that one does not arrive at any exact results by an analysis of extracts obtained with boiling solvents, whereas—and this point deserves to be stressed—the fundamental nature of thiuram vulcanization can be followed with quantitative accuracy. For this reason we shall merely present the results

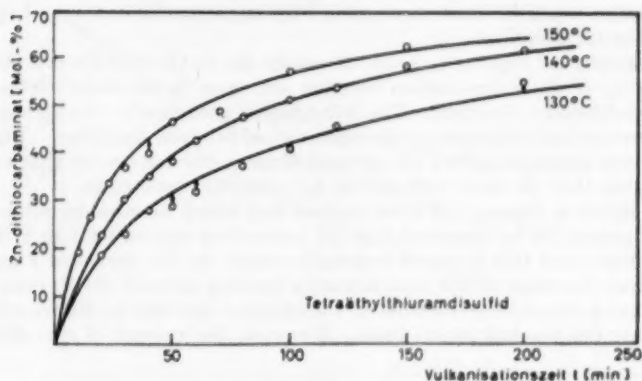


FIG. 2.—Increase of the zinc dithiocarbamate with time of vulcanization with tetraethylthiuram disulfide.

in graphical form. We shall give the detailed results in a later paper. There we shall discuss studies which make possible a more exact understanding of the observed relationships.

Figures 1, 2, and 3 show the conversion vs. temperature curves for the three thiuram disulfides. The ordinate is the yield of zinc dithiocarbamate in mole per cent of the added thiuram disulfide. The abscissa gives the vulcanization time (reaction time) in minutes. As might be expected, we find that for equal vulcanization times the fraction in percentage of the thiuram converted increases with the temperature. It is apparent that the increase is regular.

Now if, during the vulcanization, thermal decomposition of the thiuram disulfide occurred, it is hardly likely that such a clean-cut nesting of the curves would be found. Certainly it should in any case not be observed in the vulcanization of rubber with tetramethylthiuram disulfide, which is definitely the most thermally unstable of all the thiuram disulfides. From this we may conclude that, in view of the clean-cut sequence of the conversion curves, the true

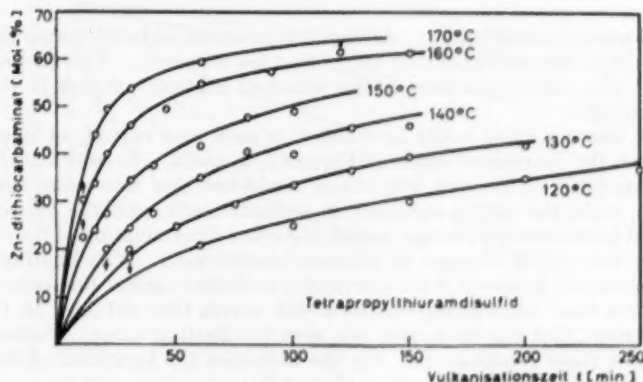


FIG. 3.—Increase of the zinc dithiocarbamate with time of vulcanization with tetrapropylthiuram disulfide.

vulcanization reaction is not accompanied by any appreciable thermal splitting of the thiuram disulfides.

Comparison of Figures 1, 2, and 3 clearly shows the well known fact that the velocity of the vulcanization reaction decreases in the order: tetraethyl-, tetrapropylthiuram disulfide. The substituents attached to the nitrogen also have a pronounced influence on the reactivity of thiuram disulfides. However, they do not appear to affect the general slope of the curves, so that one can assume that they all react with rubber by a similar mechanism.

The curves in Figures 1-3 show another fact which we consider remarkable. It is, of course, to be expected that all conversion curves tend to a limiting value. But—and this is shown especially clearly by the curves of Figure 3—it is evident that they do not tend toward a limiting value of 100 per cent, which means that a complete conversion of the thiuram disulfide to dithiocarbamate is certainly not reached in any case. However, the amount of zinc dithiocar-

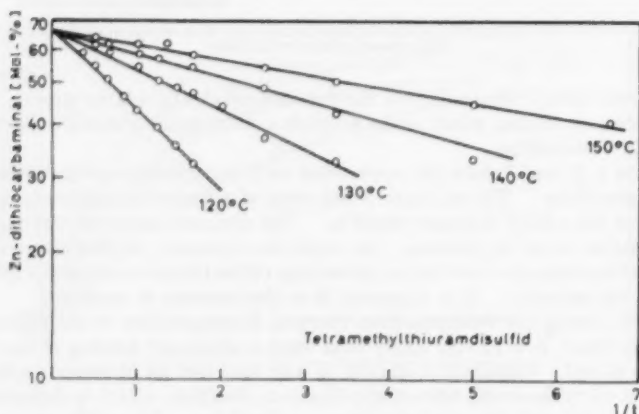


FIG. 4.—Curves for obtaining the limiting value of the yield of dithiocarbamate in the vulcanization with tetramethylthiuram disulfide. Zinc dithiocarbamate formed vs. the reciprocal of the vulcanization time.

bamate formed is considerable. At high temperatures and with longer times of vulcanization, conversions of over 60 per cent are observed. This confirms the fact that zinc dithiocarbamate is the principal reaction product in thiuram vulcanization.

What limiting value might be reached in each case cannot, of course, be found from the conversion curves of Figures 1, 2, and 3. Even the analysis of vulcanizates heated for very long times would not give this value with any certainty, since the curves approach it asymptotically, and the unavoidable analytical errors would no longer permit the exact determination of the eventually only very slight changes in dithiocarbamate yield. The limiting value can be estimated, however, if the conversion is plotted against the reciprocal of the reaction time $1/t$. Extrapolation of the curves thus obtained to $1/t = 0$ ($t = \infty$) must, if it can be carried out, give the limiting value. Figures 4, 5, and 6 show these relationships. On the ordinates the logarithm of the concentration of the dithiocarbamate is plotted in mole-per cent of the converted thiuram disulfide. The logarithm is used because, if the actual values are

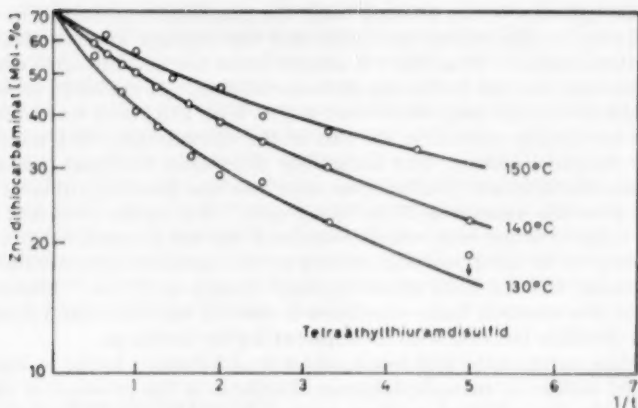


FIG. 5.—Zinc dithiocarbamate formed in the vulcanization with tetraethylthiuram disulfide vs. reciprocal of vulcanization time.

plotted, the curvature is at times so pronounced that extrapolation cannot be safely attempted. But, even with semilogarithm plots, the curves are in part more or less bent toward the abscissa (very markedly with tetrapropylthiuram disulfide and at low temperatures, Figure 6). At times, however, they are practically straight lines (Figures 4 and 6, tetramethylthiuram disulfide, and at higher temperatures tetrapropylthiuram disulfide). Even with this method of plotting, extrapolation would encounter difficulties because of the curvature that still persists, were it not for the fact that the curves of each graph show that they all tend toward one and the same limiting value. This can be seen especially clearly from Figures 4 and 6. Surprisingly enough, the limiting value is in every case independent of the temperature. Not only is independence of the limiting value of the temperature found, but, in addition, it turns out that it does not seem to depend on the particular constitution of the thiuram disulfide,

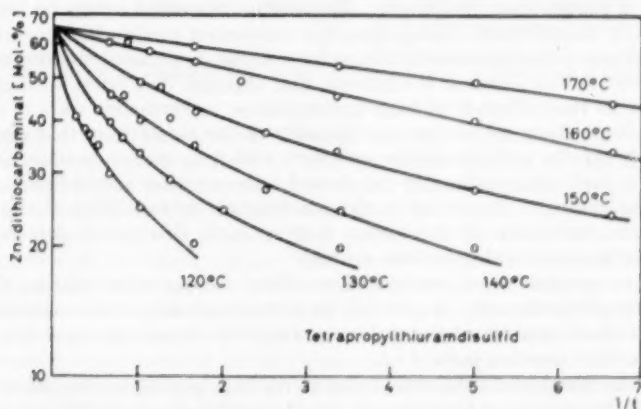


FIG. 6.—Zinc dithiocarbamate formed in the vulcanization with tetrapropylthiuram disulfide vs. reciprocal of vulcanization time.

nor—although this is not evident from the graphical representation—on its concentration in the rubber, provided that the changes in concentration are kept within bounds. Thus there is always found one and the same conversion of the thiuram disulfide to the zinc dithiocarbamate. It amounts, according to our extrapolation, to about 66 per cent or $\frac{2}{3}$. With this result we confirm what Jarrijon has already claimed in the case of the vulcanization with tetramethylthiuram disulfide, namely, that invariably practically the same proportion of the tetramethylthiuram disulfide goes over into zinc dimethyldithiocarbamate. Jarrijon gives the amount as 70 to 76 per cent. We, on the contrary, find the smaller value of 66 per cent, which, because of our more comprehensive results, we consider to be more probable as long as the question of its dependence on concentration has not been unambiguously cleared up by us. Moreover, we show that this constant finite conversion is reached not only with tetramethylthiuram disulfide but also with its adjacent higher homologs.

We thus arrive at the first result, which is as follows. In the vulcanization of natural rubber by tetraalkylthiuram disulfides in the presence of an excess of zinc oxide, the principal reaction product is always zinc dialkyldithiocarbamate, and the maximum attainable conversion to zinc dialkyldithiocarbamate of each tetraalkylthiuram disulfide in the vulcanization of rubber is 66 per cent and this is independent of the temperature and the amount present.

Without at this time discussing the question of what becomes of the rest of the thiuram disulfide, there is already, in our opinion, a further conclusion that can be drawn from this result.

It has already been pointed out that it is improbable that any of the thiuram disulfides experience thermal splitting under the conditions prevailing during vulcanization. The fact that the conversion of the thiuram disulfides is independent of both the temperature and the constitution of the particular thiuram disulfide now seems positively to exclude thermal decomposition. For if we were to suppose that, accompanying the direct reaction of the rubber with the thiuram disulfide, there also occurred a thermal splitting which could finally result in the formation of tetraalkylthiourea, carbon disulfide, and sulfur, then we would have two competing reactions to discuss, even without considering the different energies of activation. Thus the temperature-independent conversion of the thiuram disulfides to dithiocarbamate could hardly be found.

Finally, under these assumptions, the conversion would also depend on the constitutions of the thiuram disulfides, for without doubt their thermal stability is different. Now, since it is apparent that thiuram disulfides, although very sensitive to the influence of high temperatures, nevertheless do not undergo any decomposition, we are led provisionally to the assumption that they react relatively rapidly with the rubber and form with it a reaction product that represents a preliminary stage of the actual vulcanization (cross-linking of the molecular chains). According to this mechanism, the formation of zinc dithiocarbamate could also be the slower reaction, and this would determine the speed of the actual vulcanization process.

In our opinion these considerations show, among other things, that the experimental results can, in general, be understood only if one assumes that, as far as the formation of the dithiocarbamate is concerned, there is a single, self-contained reaction path.

Further insight into the vulcanization reaction of thiuram disulfides can be gained if the amount of free thiuram disulfide still present at different stages in the individual vulcanizates is determined quantitatively in the manner de-

scribed. In Figure 7 results are shown which are derived from analyses of several series of experiments with tetrapropylthiuram disulfide. The ordinates are the proportions of disulfide in mole-per cent still present, the abscissa gives the vulcanization time in minutes.

It is easy to see that the thiuram concentration in the rubber falls off rapidly with time and approaches a limiting value asymptotically. This shows, moreover, that no equilibrium prevails between thiuram disulfide, rubber, and dithiocarbamate. Note that, even at the lowest of the vulcanization temperatures chosen (120°C), the drop in thiuram concentration is still quite steep. This temperature is not capable of effecting any significant decomposition of tetrapropylthiuram disulfide, which our experiences have shown to be relatively stable. It must, therefore, be concluded that the curves of Figure 7 represent the reaction of the rubber with the disulfide.

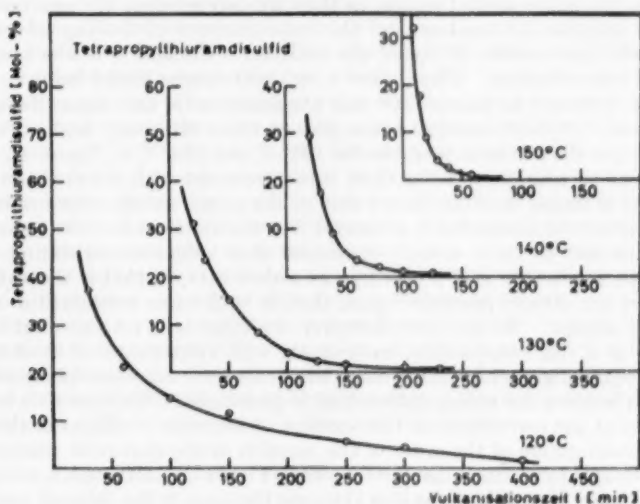


FIG. 7.—Decrease of tetrapropylthiuram disulfide (in mole-per cent) with the vulcanization time at different temperatures. Results of extraction with boiling cyclohexane over a substratum of dilute HCl.

Comparison of Figures 3 and 7 brings out the following fact. After a vulcanization time of 60 minutes at 120°C , 21 per cent of the tetrapropylthiuram disulfide has been converted into zinc dithiocarbamate, and 21.5 per cent remains uncombined in the rubber, so that, provided no other transformations have taken place, in all about 78.5 per cent of the disulfide has entered into reaction with the rubber during this time, and of this, 21 per cent has gone over into zinc dithiocarbamate. After 160 minutes at the same temperature, only 10 percent of free thiuram disulfide is still found. Therefore 90 per cent of the disulfide has interacted with the rubber. At the same time, however, the zinc dithiocarbamate content of the vulcanizate has only risen to 26 per cent; that is, it has attained only half of its limiting value of 66 per cent. Even when practically no disulfide can be still demonstrated to be present in the vulcanizates the concentration of the zinc dithiocarbamate has still not reached

its maximum value. Such considerations can be multiplied. They seem to confirm the supposition expressed above that the thiuram disulfide interacts relatively fast with rubber. In any case it looks as if the thiuram disulfide reacts with the rubber more rapidly than its assumed and relatively unknown reaction product with rubber, dithiocarbamic acid, and therefore forms zinc dithiocarbamate.

Results like those reported here are in and of themselves capable of giving an insight into the kinetics of the thiuram vulcanization. It should, therefore, be possible to obtain the order of the reaction as well as the velocity constants and, finally, from the temperature dependence of the velocity constants, the activation energies of the two reactions, which are now distinguishable from each other, namely, the formation of the zinc dialkyldithiocarbamate and the conversion of the thiuram disulfide with the rubber. This latter manifests itself clearly by the decrease of the thiuram concentration. We must point out here that the experimental results, as they are derived from the analyses of the extracts obtained by treatment of the vulcanizates with boiling solvents, are admittedly not capable of laying the basis for a discussion of the kinetics of thiuram vulcanization. This is shown by observations stated below.

First, it should be pointed out that the analyses for zinc thiocarbamates in vulcanizates of short reaction times give at times strikingly high values (for example, see the conversion curves for 120° C and 130° C in Figure 3), so that it is not at all possible to bring them into agreement with the analyses of vulcanizates of longer reaction times; that is, the points on the conversion curves cannot always be connected in a manner free of objections to form a closed arc. From this fact we have already concluded that vulcanization during the hot extraction is possibly still proceeding at a slow rate, so that if the extraction times are not always precisely equal, then in such cases irregularities must of necessity appear. In any case, however, we must take into account the fact that yields of dithiocarbamate, particularly with vulcanizates of short reaction times, are too high, while on the other hand this error must become smaller and smaller the more the vulcanization time is prolonged. We were able to assure ourselves of the correctness of this concept of the state of affairs in the course of the investigation of the order of the reaction of the change of concentration of the tetrapropylthiuram disulfide shown in Figure 7. Although not especially demonstrated here, it looks as if in this case the drop in the thiuram concentration with time, at any rate over a rather wide interval of the vulcanization, is a reaction of the first order. We also found, however, that when the analytical results were plotted in a manner corresponding to the existence of a reaction of the first order (still a straight line in the initial portion), extrapolation to a reaction time $t = 0$ gave smaller values than 100 per cent for the original concentration of the thiuram disulfide. That appears to indicate a higher conversion during part of the time. The amount of thiuram disulfide found is too low.

In a later publication we shall describe how we arrived at results which justify our discussion of the question of the kinetics of thiuram vulcanization. One can see how careful one must be in evaluating investigations in which the extraction of the vulcanizates with boiling solvents has been performed. In the past, this may not have been sufficiently taken into account. In connection with thiuram vulcanization, the hot extraction affects, however, only the exactness of the results, but not the validity of the fundamental insights obtained in the course of this investigation. Thus for example, the limiting value of the

yield of zinc dithiocarbamate, which in our case consistently amounted to 66 per cent of the thiuram disulfide originally added, is completely unaltered by the circumstances.

In conclusion, if any generalizations are to be made with regard to the question of what has become of the thiuram disulfide not accounted for (this amounts to one third of the original quantity) it should first of all be noted that our investigations have given no evidence whatever of the formation of thiuram monosulfide. We can, therefore, not share the prevailing opinion that thiuram monosulfide is formed in thiuram vulcanization, but can instead support the results of the investigation of Jarrijon, according to which thiuram monosulfide either is not formed at all or in, at most, quantities of decidedly minor order. Thus one arrives at the conclusion that zinc dithiocarbamate very probably is the sole reaction product of thiuram vulcanization. It may, therefore, also be supposed that the portion of the thiuram disulfide which has not gone over into zinc dithiocarbamate remains in the vulcanizate attached to the rubber in some, as yet unknown, manner. In fact, Jarrijon has already pointed out that rubber compounds vulcanized with tetramethylthiuram disulfide contain sulfur, and this fits. With regard to results of systematic quantitative analyses of the sulfur in extracted thiuram vulcanizates we cannot at present report, and therefore cannot take a definite position with respect to this question. Yet it is proper to mention that, on the strength of exploratory studies, the sulfur content in extracted vulcanizates of short reaction times is definitely higher than in those which have been subjected for a long time to the particular reaction temperatures. This again indicates that vulcanization by thiuram disulfide presumably cannot depend on a cross-linking of the chain molecules by sulfur, for in this case the firmly bound sulfur of the vulcanizate should not decrease in amount with time of vulcanization but should increase. Now if no other reactions take place than those shown to be likely by this investigation, then the sum of the free sulfur, the sulfur converted to dithiocarbamate, and that in the thiuram disulfide firmly bound in the rubber (calculated from the sulfur content of the vulcanizate after extraction) should amount to 100 per cent. We shall report on this at a later time.

SUMMARY

The present paper, which is concerned with the clarification of the mechanism of thiuram vulcanization, although the studies are still in progress, nevertheless leads us to the following fundamental facts.

1. In the vulcanization of natural rubber by thiuram disulfides in the presence of excess zinc oxide, the zinc dialkyldithiocarbamate at any stage is the principal, and probably even the sole, reaction product that can be extracted with organic solvents.

2. There are no experimental proofs that make probable the presence of thiuram monosulfide in the extracts.

3. The maximum attainable conversion in vulcanization of any particular tetraalkylthiuram disulfide to the corresponding zinc dialkyldithiocarbamate amounts to about 66 per cent, and this is independent of the temperature.

4. The maximum conversion of the thiuram disulfide is practically independent of its concentration in the rubber, provided that the differences in the concentrations involved are not excessive.

5. The extracts of thiuram vulcanizates contain free thiuram disulfide in addition to the zinc dithiocarbamate. The concentration of the thiuram di-

sulfide decreases rapidly with the time of vulcanization and approaches zero asymptotically. This is exemplified by the results with tetrapropylthiuram disulfide.

6. It is shown to be probable that the vulcanization continues to proceed slowly during extraction of the vulcanizate with boiling solvents, so that the analytical results of the hot extracts are not such as to throw light on the kinetics of thiuram vulcanization.

7. The decrease of concentration of the free thiuram disulfide in the vulcanizates evidently takes place more rapidly than the formation of the zinc dithiocarbamate. It is, therefore, probable that the vulcanization of rubber by thiuram disulfides can be separated into two partial processes. There is a rapid reaction of the rubber with the thiuram disulfide, which is presumably "vulcanization-inert", and there is an additional, slower reaction which involves a splitting off of dithiocarbamic acid from a reaction product between rubber and thiuram disulfide and which leads to the vulcanization.

8. All exhaustively extracted vulcanizates contain sulfur. Apparently the sulfur content in vulcanizates of short reaction times is greater than in those of longer periods of vulcanization.

9. The formation of the zinc dithiocarbamate as sole reaction product in the thiuram vulcanization can hardly be explained otherwise than as a dehydrogenation of the rubber, concerning the mechanism of which we still know, to be sure, scarcely anything. It is reasonable to conceive of a reaction of the disulfides with the α -methyl groups, in which chain radicals may be formed which give rise to cross-linking over C—C bonds.

The investigations are being continued and a further communication will appear in the near future.

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II. VULCANIZATION OF NATURAL RUBBER WITH THIURAM DISULFIDES

PART 2

STATEMENT OF THE PROBLEM

In a recently published paper¹ we reported on a number of basic conclusions which could be drawn from the results of analytical investigations of the conversion of materials in the vulcanization of natural rubber by thiuram disulfides.

The principal, if not the sole, reaction product, was generally a dialkyldithiocarbamic acid, which combines with the zinc oxide, present in all the formulations, to form zinc dithiocarbamate. If this were not the case, there would be further decomposition and the course of the reaction involved in this process would presumably be complicated². The maximum yield of zinc dithiocarbamate was practically independent of the temperature of vulcanization as well as of the particular constitution of the thiuram disulfide. In our experiment, it amounted to about 66 per cent in every case. According to our experience so far, the yield cannot vary significantly with the concentration of the thiuram disulfide in the rubber, specifically, for example, when the amount of thiuram disulfide is doubled. Tetraalkylthiuram monosulfides could not be found in the extracts of the vulcanizates. All the results appeared to indicate

TABLE I

VULCANIZATION OF NATURAL RUBBER WITH TETRAMETHYLTHIURAM DISULFIDE

Comparative results obtained by hot extraction with acetone (h) and by cold extraction with ethyl acetate (c). The data on the thiuram disulfide and zinc dithiocarbamate are in mole-per cent of the initial thiuram disulfide.

87° C				120° C				130° C			
Cure (min.)	Mole-% thiuram (c)	Mole-% ZnDTC (c)		Cure (min.)	Mole-% thiuram (c)	Mole-% ZnDTC (c)	Mole-% ZnDTC (h)	Cure (min.)	Mole-% thiuram (c)	Mole-% ZnDTC (c)	Mole-% ZnDTC (h)
360	59.9	14.6		30	41.5	16.8	37.3	20	34.1	19.1	34.5
600	41.9	22.8		40	28.1	24.2	36.2	30	22.7	27.2	33.2
900	27.8	28.0		50	21.2	26.3	39.7	40	14.1	33.9	37.3
1080	21.2	33.1		60	15.6	30.8	32.7	60	7.7	43.5	47.8
1260	17.1	37.5		80	9.4	39.2	39.6	80	5.7	49.3	51.0
1500	10.6	40.6		100	7.8	42.8	43.6	100	4.8	(46.9)	55.3
1800	7.7	45.1		150	5.6	50.8	51.7	120	4.3	54.1	—
2400	3.8	49.9		200	5.1	54.3	55.5	150	3.8	57.1	59.2
				300	—	—	59.4	200	3.5	62.1	64.6

140° C				150° C			
Cure (min.)	Mole-% thiuram (c)	Mole-% ZnDTC (c)	Mole-% ZnDTC (h)	Cure (min.)	Mole-% thiuram (c)	Mole-% ZnDTC (c)	Mole-% ZnDTC (h)
10	36.0	15.2	33.1	10	19.8	25.1	34.9
15	24.7	23.6	32.1	15	14.3	34.3	41.3
20	16.6	27.9	33.4	20	11.7	39.2	45.4
30	9.6	33.3	42.9	30	6.5	50.2	51.2
40	6.7	42.7	49.6	40	5.5	54.8	55.0
60	4.7	52.5	54.7	60	2.7	57.1	58.3
80	3.2	57.0	57.7	80	2.7	60.5	62.4
100	2.6	58.2	59.0	100	2.2	61.5	62.1
150	2.3	61.6	62.3	150	1.5	65.7	63.7
200	1.9	62.2	62.3				

TABLE 2

VULCANIZATION OF NATURAL RUBBER WITH TETRAETHYLTHIURAM DISULFIDE

Comparative results obtained by hot extraction with acetone (h) and by cold extraction with ethyl acetate (c). The data on the thiuram disulfide and zinc dithiocarbamate are in mole-per cent of the initial thiuram disulfide.

120° C			130° C			140° C			
Cure (min.)	Mole-% thiuram (c)	Mole-% ZnDTC (c)	Cure (min.)	Mole-% thiuram (c)	Mole-% ZnDTC (c)	Cure (min.)	Mole-% thiuram (c)	Mole-% ZnDTC (c)	Mole-% ZnDTC (h)
30	69.3	9.4	20	54.9	12.8	15	45.4	14.2	21.5
40	60.5	13.0	30	42.8	22.1	20	34.7	17.7	22.9
60	47.0	17.0	40	31.4	24.4	30	23.4	25.5	30.8
80	36.4	19.8	50	25.2	27.8	40	16.5	32.6	35.1
100	28.5	26.5	60	20.0	31.1	50	13.3	36.7	38.7
120	20.5	28.4	80	14.1	36.2	60	12.0	42.1	43.0
160	17.4	34.9	100	11.7	40.4	80	8.3	47.1	48.2
200	15.8	36.7	120	9.6	43.2	100	6.7	52.9	53.0
240	14.7	40.7	150	9.0	47.1	150	5.6	55.8	61.3
			200	8.0	48.8	200	4.7	58.4	64.3

150° C			
Cure (min.)	Mole-% thiuram (c)	Mole-% ZnDTC (c)	Mole-% ZnDTC (h)
10	36.6	16.4	18.8
15	20.7	24.2	26.8
23	13.8	31.9	34.0
30	9.8	38.4	37.3
40	8.1	40.7	41.2
50	7.3	45.1	47.1
70	5.7	50.7	47.0
100	5.0	59.0	56.8
160	3.1	63.5	—

that thiuram disulfides are hydrogenated by the rubber and are converted to dithiocarbamic acid. The chain radicals of polyisoprene which are then formed combine with the product of the cross-linking of the molecular chains through C—C bonds. Tetramethylthiuram disulfide reacts significantly faster with rubber than do its next higher homologs. All thiuram disulfides, however, enter into complete conversion with the rubber, i.e., the thiuram concentration falls progressively with increasing time of vulcanization to zero. Two reactions can be clearly distinguished. First, the thiuram disulfides react with the rubber to form an intermediate product with the allyl systems. This reaction is presumably "vulcanization indifferent". In a process which takes place more slowly, dithiocarbamic acid is split out as an intermediate product. Here the detailed steps are not definitely known. This reaction represents the actual vulcanization.

In the previous paper we pointed out that the analyses of extracts made by the use of boiling solvents are certainly not exact, and attributed this provisionally to a progressive continuation of both reactions during the "hot" extraction. Since we considered it very important to obtain results which can form a basis for a discussion of the order of the reaction, both of the decrease of the concentration of the thiuram disulfides and of the increase of the concentration of the zinc dithiocarbamates during vulcanization, we have repeated the whole investigation and carried out the extraction of the thiuram vulcanizates with acetic acid at room temperature. It was found by experience that, under these conditions, it takes 5 to 6 days. The quantitative determination

of thiuram disulfide and zinc dithiocarbamate in the extract, which was again carried out by the conductometric titration procedure developed by us, turns out to be simpler with this treatment of the vulcanizates. This is especially true in the case of the thiuram determination, which can now be carried out directly after the conductometric titration of the dithiocarbamate with acid in the same solution.

EXPERIMENTAL RESULTS

In Tables 1, 2, and 3 the analytical results of the hot and cold extracts are compared.

It is found that the extraction with boiling solvents does indeed, especially for short vulcanization times, give greater yields of zinc dithiocarbamate and consequently less thiuram disulfide than the cold extraction. This is especially

TABLE 3

VULCANIZATION OF NATURAL RUBBER WITH TETRAPROPYLTHIURAM DISULFIDE

Comparative results obtained by hot extraction with acetone (h) and by cold extraction with ethyl acetate (c). The data on the thiuram disulfide and zinc dithiocarbamate are in mole-per cent of the initial thiuram disulfide.

120° C					130° C				
Cure (min.)	Mole-% ZnDTC (c)	Mole-% thiuram (c)	Mole-% ZnDTC (h)	Mole-% thiuram (h)	Cure (min.)	Mole-% ZnDTC (c)	Mole-% thiuram (c)	Mole-% ZnDTC (h)	Mole-% thiuram (h)
30	4.6	67.6	18.7	37.5	20	4.8	63.4	19.8	30.8
60	13.1	49.0	21.1	21.8	30	10.5	50.4	20.2	23.7
100	21.1	35.3	25.1	14.8	50	19.5	38.2	24.3	15.4
150	29.0	24.0	30.0	11.3	75	27.5	25.2	29.2	8.4
200	33.5	19.0	35.1	4.2	100	32.0	19.2	33.7	3.9
250	36.1	17.4	36.9	5.3	125	35.4	12.5	36.5	2.6
300	37.8	16.0	37.8	4.4	150	38.6	10.4	39.3	2.1
400	41.0	14.2	40.8	3.5	200	42.1	6.6	41.9	1.45
700	45.5	11.6	45.6	2.1	350	49.6	4.2	46.8	1.18

140° C					150° C				
Cure (min.)	Mole-% ZnDTC (c)	Mole-% thiuram (c)	Mole-% ZnDTC (h)	Mole-% thiuram (h)	Cure (min.)	Mole-% ZnDTC (c)	Mole-% thiuram (c)	Mole-% ZnDTC (h)	Mole-% thiuram (h)
20	9.6 (?)	56.3	20.0	29.3	10	5.8	72.8	13.6	31.5
30	—	—	25.7	17.3	15	14.7	39.0	24.3	17.0
40	24.5	23.1	27.6	9.0	20	27.4	19.9	27.5	8.3
60	32.5	10.0	35.0	2.8	30	36.6	6.2	34.1	3.7
80	39.0	6.4	40.6	1.78	40	41.2	4.4	37.6	2.1
100	43.8	4.2	39.6	1.21	60	47.2	2.9	42.1	0.52
125	47.3	2.9	45.4	0.42	80	51.1	2.3	48.2	—
150	49.1	2.4	45.8	—	100	53.7	1.9	49.1	—
250	54.7	2.1	51.6	—	180	58.9	1.3	54.5	—

160° C				
Cure (min.)	Mole-% ZnDTC (c)	Mole-% thiuram (c)	Mole-% ZnDTC (h)	Mole-% thiuram (h)
10	19.0	48.0	22.3	17.9
15	29.1	11.5	33.8	5.3
20	34.8	3.1	39.8	1.6
30	44.3	2.2	46.0	0.64
45	50.7	1.5	49.6	—
60	54.2	1.3	54.9	—
90	57.9	—	57.7	—
150	61.4	—	61.3	—

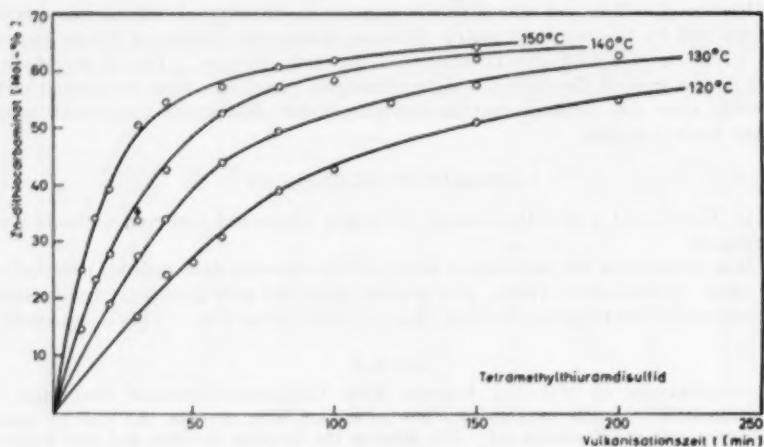


FIG. 1.—Increase of concentration of zinc dithiocarbamate (in mole-per cent of initial thiuram disulfide) vs. vulcanization time. With tetramethylthiuram disulfide.

pronounced in the vulcanization of rubber with tetramethylthiuram disulfide. It is also noted, however, that the differences become progressively less with longer times of vulcanization, and finally even vanish. Without doubt the results obtained by the analysis of the cold extracts are the correct ones.

Figures 1 through 3 show the conversion curves, namely, the increase with time of the concentration of the zinc dithiocarbamate during the vulcanization at different temperatures for all three thiuram disulfides. The individual

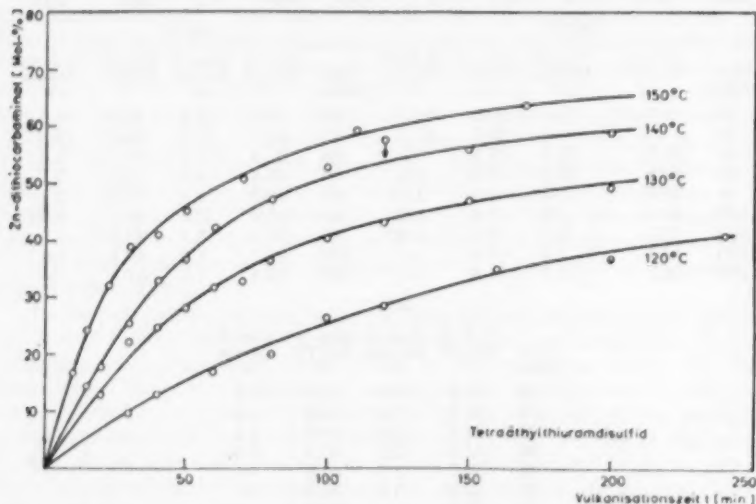


FIG. 2.—Increase of concentration of zinc dithiocarbamate (in mole-per cent of initial thiuram disulfide) vs. vulcanization time. With tetraethylthiuram disulfide.

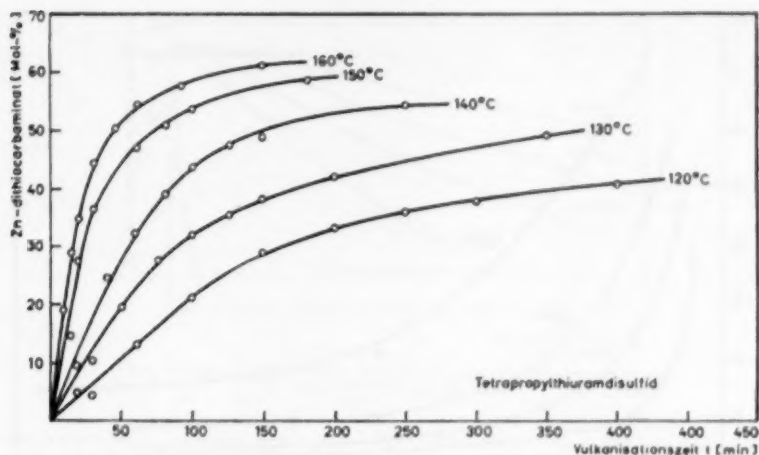


Fig. 3.—Increase of concentration of zinc dithiocarbamate (in mole-per cent of initial thiuram disulfide) vs. vulcanization time. With tetrapropylthiuram disulfide.

points can now be much more easily joined to give a continuous curve, and the slope of the curves in the region of shorter vulcanization times is not so steep.

Figures 4 through 6 show the decrease of concentration of the thiuram disulfides with the vulcanization time. Even in the case of the extremely sensitive tetramethylthiuram disulfide, the relationships can now be studied (Figure 4). The drop in concentration is steeper for the methyl derivative than for the ethyl derivative. This in turn reacts faster than tetrapropylthiuram disulfide. It can be seen that, with long vulcanization times, the thiuram concentration shows only very slight changes. The curves give one the impression that they approach the abscissa extremely slowly (decrease to zero), so that one could suppose the reaction to come to a complete standstill.

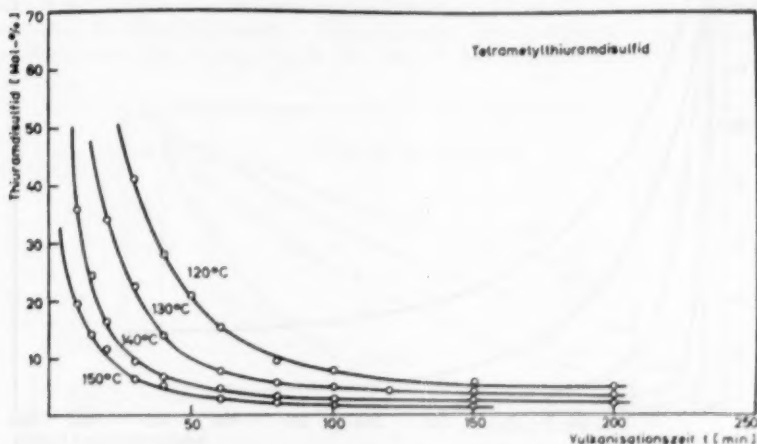


Fig. 4.—Decrease of concentration of tetramethylthiuram disulfide vs. vulcanization time.

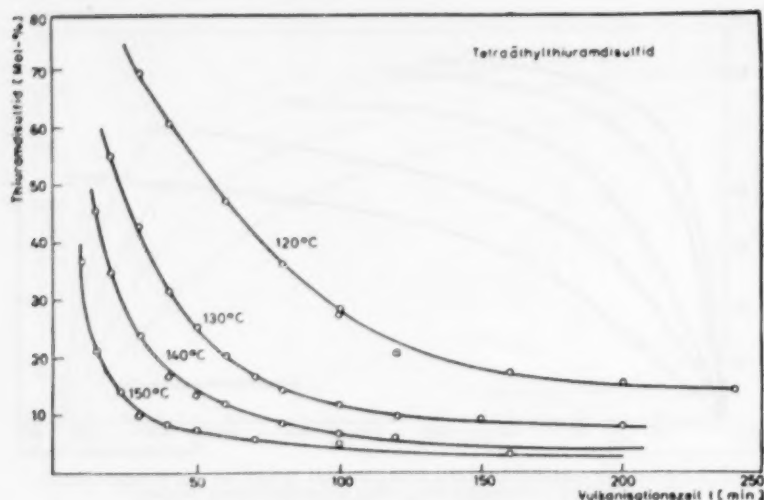


FIG. 5.—Decrease of concentration of tetraethylthiuram disulfide vs. vulcanization time.

Figures 7 through 9, in which the log of the yield (mole-per cent) of the dithiocarbamate is plotted as a function of the reciprocal of the vulcanization time, show that the cold extraction does not change the molar conversion of the thiuram disulfides to the zinc dithiocarbamate. This is always the same, i.e., practically independent of the temperature and of the constitution of the thiuram disulfide. Although the curves are somewhat wavy in parts, it is unmistakable that they all converge in the ordinate at practically the same

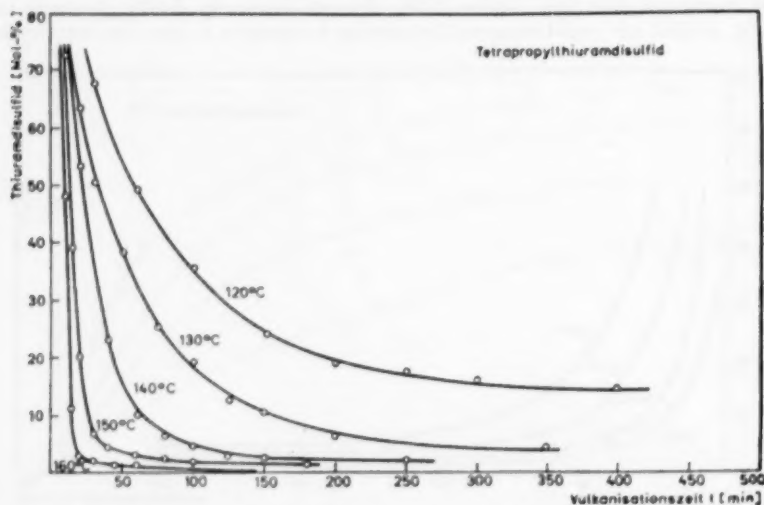


FIG. 6.—Decrease of concentration of tetrapropylthiuram disulfide vs. vulcanization time.

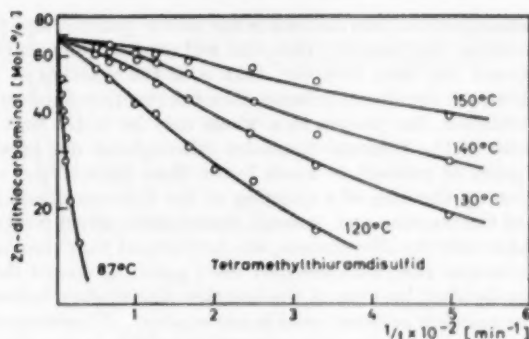


Fig. 7.—Showing the limiting value of the yield of dithiocarbamate with tetramethylthiuram disulfide.

molar conversion, namely, again at about 66 per cent. In order to remove all doubt as to the thermal stability of the thiuram disulfides under the conditions of the vulcanization, we have carried out a series of experiments with tetramethylthiuram disulfide at 87° C. Any thermal splitting of this disulfide at this temperature is practically excluded⁴. It can be seen that the conversion curve for 87° C (Figure 7) fits very well into the general picture. It rises steeply (long reaction time, small values for $1/t$) and then merges into the ordinate.

THE KINETICS OF THIURAM VULCANIZATION

It has already been pointed out that one may assume that the thiuram disulfides first react with the allyl systems in the polyisoprene chains by a high-velocity reaction, and form with these an intermediate product that represents an initial stage of the vulcanization reaction. Now in considering what information in general can be obtained from a kinetic investigation of the above case, it is not necessary to have exact knowledge of how the thiuram disulfides are bound by the allyl system. If one assumes, for example, that the thiuram disulfides enter into the reaction in the form of their radicals $R_2=N-C(S)-S^*$

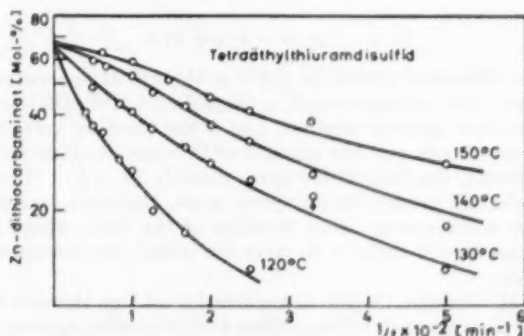


Fig. 8.—Showing the limiting value of the yield of dithiocarbamate with tetraethylthiuram disulfide.

and that the decomposition into radicals is the slower process, and therefore the one which determines the velocity, then one will expect a monomolecular reaction. If this is not the case, however, that is, if the reaction of the radicals with the allyl groups is the slower process, then the reaction must be a bimolecular one. Nevertheless, the process as a whole may be of the first order, since the concentration of the thiuram disulfides (throughout our experiments 0.1 millimole per gram of rubber) is much lower than that of the allyl groups. Even if one gives up the idea of a splitting of the thiuram disulfides as a preliminary stage of the reaction and, instead, postulates a direct interaction of the thiuram disulfides with the allyl system, one may expect that the reaction which *per se* is a bimolecular one, will manifest itself again as one of the first order (pseudo-monomolecular) because of the extreme discrepancy between the concentration of the reaction partners used in our studies. Therefore one may also assume that the decrease of the thiuram concentration in the rubber with in-

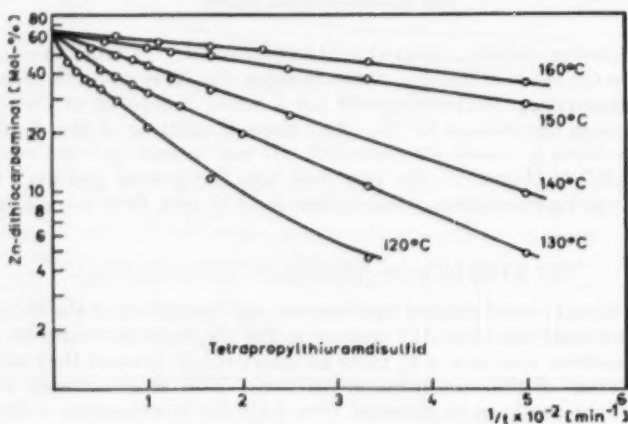


Fig. 9.—Showing the limiting value of the yield of dithiocarbamate with tetrapropylthiuram disulfide.

creasing vulcanization time will satisfy the equation for a conversion of the first order:

$$\ln(a - x) = -k \cdot t + \ln a \quad (1)$$

For the case discussed above, in (1) a is the initial concentration of the thiuram disulfide (100 mole-per cent), x the amount of disulfide converted at time t , t the reaction time in minutes, and k the reaction velocity constant. Since the analyses always give the amount of thiuram disulfide still present in the rubber at time t , the experiment gives directly $(a - x)$. The amount of thiuram disulfide still present at any time must, therefore, according to our assumptions, be a decreasing linear function of the time, whose intersection with the ordinates ($x = 0$ and $t = 0$) gives the initial concentration ($\log a = 2$ in mole-per cent).

In Figures 10 through 12, the concentration of free thiuram disulfide (in mole-per cent) found for each vulcanization time is plotted against the reaction time. It is seen that the curves for each figure come together in the ordinate 100 per cent. This is a consequence of the correspondence now established by

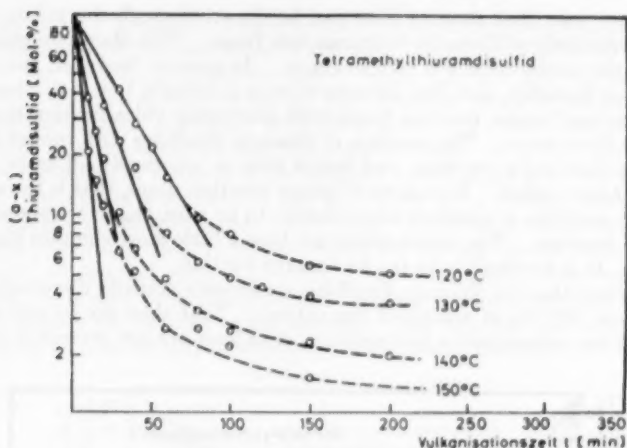


Fig. 10.—Kinetics of the decrease of thiuram concentration with time of vulcanization. Tetramethylthiuram disulfide.

the cold extraction between conversion and reaction time. The general character of the curves is in all cases similar. The higher the temperature, the more rapidly the curves fall off, and in this respect a difference can be recognized between the three thiuram disulfides. The decrease is steepest with tetramethylthiuram disulfide; it is already less pronounced with tetraethylthiuram disulfide. As already pointed out, the tetrapropylthiuram disulfide reacts the most slowly. This is not very clearly seen by comparing Figure 12 with Figures 10 and 11, since the scale along the abscissa in Figure 12 is smaller than in the other two.

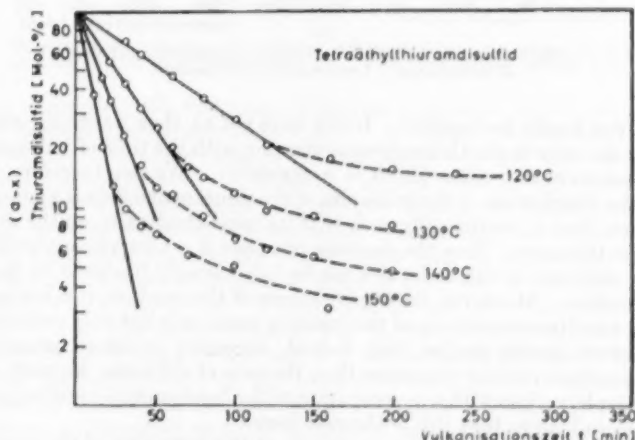


Fig. 11.—Kinetics of the decrease of thiuram concentration with time of vulcanization. Tetraethylthiuram disulfide.

It is now seen that straight lines can be drawn through the points in the region of relatively still smaller vulcanization times. This shows up especially clearly in the curves for lower temperatures. In general, however, the curves depart from linearity, and this departure from a straight line is displaced toward longer and longer reaction times with decreasing vulcanization temperature in all three cases. The reaction of thiuram disulfides with rubber is thus certainly a first-order reaction, and this is true in practically all cases over a 50 per cent conversion. In regions of longer reaction times, that is toward the end of the reaction, it proceeds more slowly, to be sure, than corresponds to a first-order reaction. The relationships are thus a little more complex than was expected. It is worthwhile to try to account for this.

We believe that the thiuram disulfides are already actually dissolved at the temperature (50° C) of mixing of the rubber. That they are in any case in solution at the vulcanization temperature, or at least are not present in crystal-

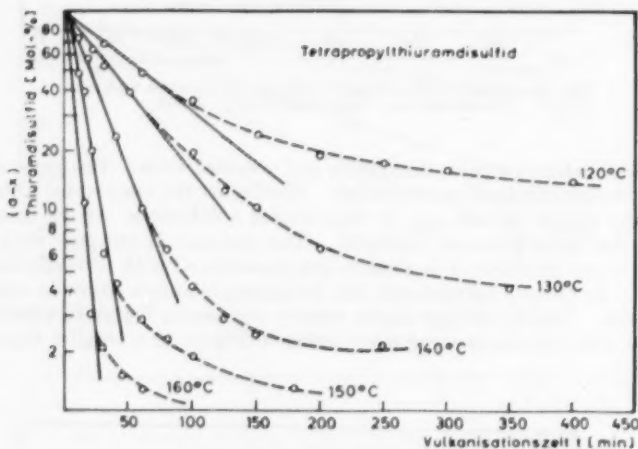


Fig. 12.—Kinetics of the decrease of thiuram concentration with time of vulcanization. Tetrapropylthiuram disulfide.

line form, can hardly be doubted. If this were not so, then we should certainly expect the decrease in the thiuram concentration with the time of vulcanization to be a reaction of zero order ($dx/dt = a \cdot \text{constant}$). We can, therefore, postulate that the distribution of the molecules of the thiuram disulfide is a completely random one, that is, statistically such that its concentration is, on the average, everywhere the same. Now the reaction proceeds in a very viscous medium in which the diffusion of the molecules can be considerably hindered by the high internal friction. Moreover, during the course of the reaction, it is not possible to effect a simultaneous mixing of the reacting mass, as is not only customary in other reaction kinetic studies, but, indeed, necessary standard practice. If now, the reaction velocity is greater than the rate of diffusion, we must, in the above example, reckon with a degeneration of the fundamental reaction process. We are led to believe that this is the case here.

One may picture a mechanism in which, at the beginning of the reaction, a number of molecules or radicals of the thiuram disulfide are in an arrangement

("constellation") favorable to conversion. Other molecules or radicals, however, must first arrive at this state by diffusion, the more so since the longer the reaction has been in progress, the more frequently they will encounter allyl systems which have already reacted. This seems to us the explanation of the fact that the reaction is initially of the first order, but toward the end, departures from this are observed and it becomes slower. One can, perhaps say, that the molecules or radicals of the thiuram disulfide are not "supplied" fast enough to maintain a conversion like that given by a reaction that proceeds initially as one of the first order. Now, since the molecules of the thiuram disulfides in the rubber that are still not converted are still free to move, they will eventually all interact with the rubber. However, this process will become slower at the longer vulcanization times, because diffusion becomes the factor that determines the velocity of the reaction. The effect of this is to make the curves drop off considerably more slowly to zero concentration than a first-order

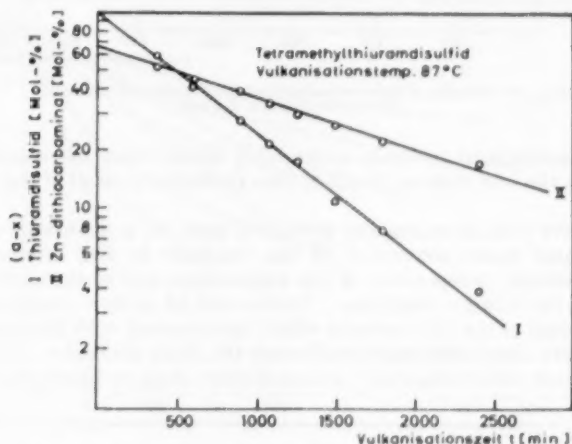


FIG. 13.—Kinetics of the decrease of the thiuram concentration (I), and increase of dithiocarbamate concentration with time of vulcanization (II). Tetramethylthiuram disulfide at 87° C.

reaction demands. We find support for this view in the fact that the conversion of tetramethylthiuram disulfide at 87° C (curve 1 in Figure 13) is of the first order over the whole range of reaction times. In this case we must conclude that the reaction of the thiuram disulfide with the allyl system in the polyisoprene is what determines the velocity during the entire course of the reaction; in other words, at this temperature the diffusion can always keep up with the conversion, because this occurs much more slowly than at the higher temperatures. A somewhat similar effect is observed in the kinetics of the formation of dithiocarbamate⁵ (Figures 14 through 16). Here too it is to be noted that, after the initial course of the reaction, which is of the first order, departures from it occur in the region of longer reaction times. These relationships can be explained on the basis of the same considerations as those developed to account for the decrease of the thiuram concentration. The dithiocarbamate formation at 87° C is, likewise, a reaction of the first order over the whole range of the particular times of vulcanization (Curve II in Figure 13). It can now be seen very well (Figure 13) that the formation of dithiocarbamate

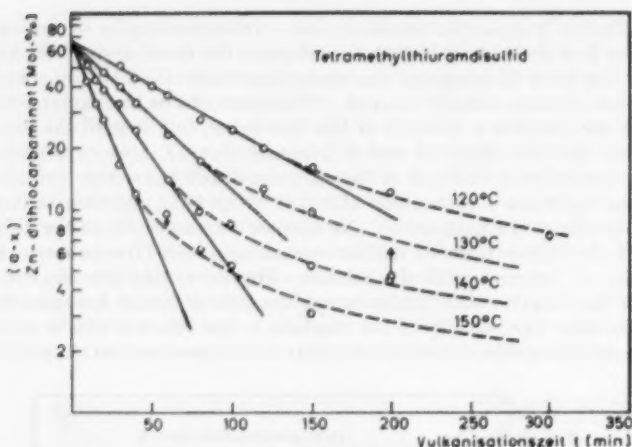


Fig. 14.—Kinetics of dithiocarbamate formation during vulcanization.
Tetramethylthiuram disulfide.

(actual vulcanization) proceeds appreciably slower than the reaction of the rubber with the free thiuram disulfide (the preliminary stage of the vulcanization).

The above considerations also provide a basis for a discussion of the consistently equal molar conversion of the disulfides to zinc dithiocarbamate. This is practically independent of the temperature and of the particular constitution of the thiuram disulfides. To this end let us now postulate that the atom groupings of the allyl systems which have reacted with thiuram disulfide and which are distributed statistically over the chain molecules of the polyisoprene will react with residual allyl groups of other chain molecules (intermolecu-

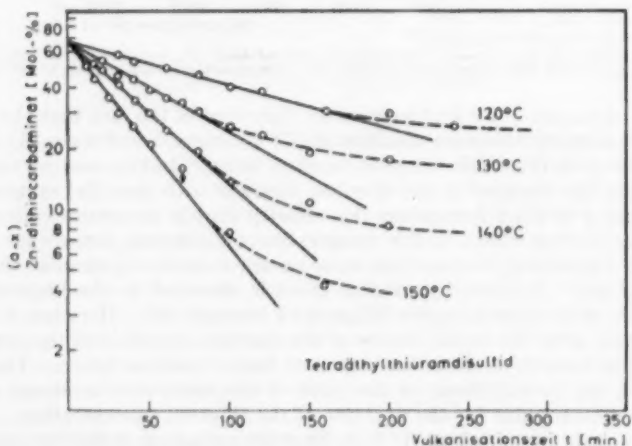


Fig. 15.—Kinetics of dithiocarbamate formation during vulcanization.
Tetraethylthiuram disulfide.

lar) or those of the same chain molecules (intramolecular). For this conversion, as new considerations show, the mobility of the chain segments is important, that is, the micro-Brownian movement. This is so because each thiuram disulfide which has reacted with the rubber and is, therefore, no longer free but firmly attached to discrete positions in the chain molecule, is able to change its position only to the extent permitted by the micro-Brownian movement. This would mean, however, a considerable reduction, when compared with the free molecules of the thiuram disulfide, of the configurations favorable to further conversion. The change of position of firmly bound thiuram disulfide, that is, at the same time the change of position of the allyl groups of a polyisoprene chain to which they are bound, must be considered to be restricted, and it would, moreover, be decreased if at positions of cross-linking. The final outcome would then be that individual allyl groups saturated by thiuram disulfide

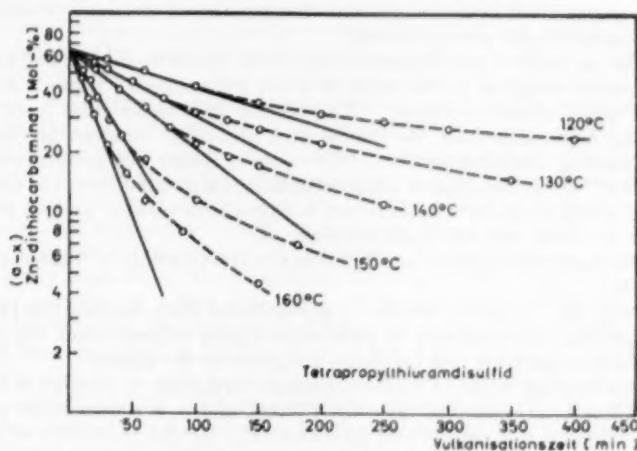


Fig. 16.—Kinetics of dithiocarbamate formation during vulcanization. Tetrapropylthiuram disulfide.

can no longer enter into reaction (the vulcanizates contain firmly bound sulfur), because they no longer encounter in their environment any free allyl groups in a configuration favorable to the reaction. The reaction will be arrested because of steric hindrance. If it were not for this, it could proceed to eventual complete conversion of all the thiuram disulfide to zinc dithiocarbamate, since this is possible according to the basic chemistry.

In this way it is possible to account for the practically constant conversion of thiuram disulfides to dithiocarbamate, which at any given thiuram concentration is also a sterically hindered reaction which is independent of the temperature. It is evident that it cannot be brought into direct correspondence with the chemistry of the vulcanization reaction, but rather can be explained by considering the inner structure of the polyisoprene (i.e., as a micromolecular, felt-like structure). If our concept is correct, however, then as a consequence the final yield of dithiocarbamate must be somewhat dependent on the concentration. Studies of this point are under way.

If Jarrijon's work⁶ on thiuram vulcanization is referred to, it will be noted that our kinetic studies of the reaction of rubber with thiuram disulfides lead to the same interpretation as those stated by Jarrijon. He characterized the vulcanization of rubber with tetramethylthiuram disulfide as a reaction that "proceeds statistically", an idea which we have undertaken in this paper to interpret more in detail on the basis of our quantitative results. We have expounded our ideas at some length because we are convinced that we shall encounter similar relationships in the investigation of other vulcanization reactions. Our interpretation can hardly be expected to be unconditionally correct, but provisionally we believe all the experimental material supports it. These investigations are being continued.

SUMMARY

This paper gives some insight into the kinetics of thiuram vulcanization. The following results were obtained.

1. The decrease of concentration of thiuram disulfides during vulcanization is a first-order reaction in the range of short vulcanization times. At longer reaction times, departures occur. The process then takes place more slowly.

2. The departures from the course of a first-order reaction are displaced with decreasing temperature toward the range of longer vulcanization times.

3. At 87° C, the reaction of tetramethylthiuram disulfide is of the first order over the whole range of vulcanization temperatures chosen, and at this temperature no deviations whatever are observed.

4. The same relationships are found in the kinetic study of dithiocarbamate formation.

5. From the combined results, it is concluded that, besides the two reactions occurring independently of each other during vulcanization, the diffusion of the reaction partners also has some influence on the kinetics.

6. The limiting value of dithiocarbamate formation is correlated with the macromolecular structure of the polyisoprene, and it is shown to be probable that this limit is not determined fundamentally by the chemistry of the vulcanization reaction.

ACKNOWLEDGMENTS

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- ² The conversions presumably undergone by tetramethylthiuram disulfide in the vulcanization of rubber in the absence of zinc oxide have been discussed by Craig and coworkers (*J. Polymer Sci.*, **8**, 321 (1952)). According to these authors, the secondary amine resulting from the decomposition of the free dithiocarbamic acid would split any tetramethylthiuram disulfide that still remains.
- ³ Scheele and Gensch, *Kautschuk u. Gummi*, **6**, WT 147 (1953).
- ⁴ From the literature one learns that pure tetramethylthiuram disulfide undergoes extremely slow thermal splitting below 100° C.
- ⁵ In Figures 14, 15, and 16, the ordinates give the log of the difference between the limiting value of the dithiocarbamate yield (66 per cent) and the amount of the dithiocarbamate found by analysis for time t (both in mole-per cent of the initial thiuram disulfide). This explains the decreasing function.
- ⁶ Jarrijon, *RUBBER CHEM. & TECHNOLOGY*, **19**, 1061 (1946).

III. VULCANIZATION OF NATURAL RUBBER WITH THIURAM DISULFIDES

PART 3

THE ENERGY RELATIONSHIPS IN THIURAM VULCANIZATION

The specific purpose of this paper is to amplify and complete Part II of our series on "The Vulcanization of Natural Rubber with Thiuram Disulfides", in which the kinetics of the material conversion of this vulcanization reaction was treated¹. Although kinetic analyses of the course of reactions do not always furnish the key to their complete understanding, they do, in general, make it possible to characterize the basic chemistry involved and to mark out the framework within which discussions of details are to be contained. This has proved to be true in the study of the kinetics of thiuram vulcanization.

It turned out that the experiments indicated that two reactions must be distinguished. One is an interaction of the thiuram disulfides with the allyl units of the polyisoprene. This one is presumably "vulcanization indifferent". The other is the splitting off of dithiocarbamic acid from the reaction product of the thiuram disulfides with the allyl groups. This leads to actual vulcanization. The first of the two reactions takes place more rapidly than the second. The kinetic analysis thus requires the assumption of an intermediate product in thiuram vulcanization, about the constitution of which, to be sure, we cannot make any clear statement. Both reactions are of the first order up to a conversion considerably in excess of 50 per cent². Finally, however, they proceed considerably more slowly than would be required by the process which at first proceeds according to a first-order rate. This was attributed to limited diffusion of the reaction partners in the highly viscous medium "rubber". This concept was confirmed by the fact that, at lower temperatures, both reactions are of the first order over the whole range of the vulcanization temperatures chosen for observation. It is reasonable to interpret this with the assumption that from this point on the diffusion occurs more rapidly than the reaction itself. The concentration of those molecules of thiuram disulfide which can still move freely in the rubber decreases progressively with the time of vulcanization, and in the completely reacted vulcanizates there is practically no residual thiuram disulfide. This indicates that all the thiuram disulfide enters into reaction with the rubber. The concentration of the dithiocarbamate formed during the course of the vulcanization, however, attains a limiting value that is independent of the temperature and the particular constitution of the thiuram disulfide. This limiting value is less than 100 per cent (calculated on the amount of thiuram disulfide added) and amounted to about 66 per cent in our experiments. This result shows especially clearly that we are dealing with two reactions, and leads to the conclusion that not all the allyl units of bound thiuram disulfide contribute to the cross-linking of the elementary molecules. Instead, the actual vulcanization reaction finally comes to a stop because of steric hindrance. This finds its explanation in the macromolecular structure of the rubber. The vulcanization itself must thus depend on a dehydrogenation of the rubber (production of dithiocarbamic acid). The chain radicals formed combine so that a cross-linking of the elementary molecules through C—C bonds results. In the light of this interpretation, there are many analogies between the reaction of thiuram disulfides and that of *tert*-butyl peroxide with rubber.

TABLE 1

RATE CONSTANTS OF THE REACTION OF TETRAMETHYLTHIURAM DISULFIDE WITH NATURAL RUBBER (k_{TD}) AND OF THE FORMATION OF THE DIMETHYLDITHIOCARBAMATE (k_{DC})

87° C			120° C			130° C		
Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$	Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$	Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$
360	1.43	6.83	30	2.93	0.97	20	5.37	1.58
600	1.45	6.98	40	3.17	1.12	30	4.94	1.72
900	1.42	6.08	50	3.10	1.00	40	4.89	1.77
1080	1.44	6.35	60	3.10	1.03	60	(4.27)	1.76
1260	1.41	6.53	80	2.95	1.10	80	(3.58)	1.68
1500	1.50	6.29	100	2.55	1.03	120	(2.62)	1.39
1800	1.43	6.27	150	(1.92)	0.96	150	(2.18)	1.29
2400	(1.36)	(5.77)	200	(1.48)	(0.85)	200	(1.68)	1.33

140° C			150° C		
Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$	Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$
10	10.20	2.58	10	1.62	4.69
15	9.30	2.91	15	(1.30)	4.80
20	9.00	2.70	20	(1.07)	4.42
30	(7.80)	2.30	30	(0.91)	4.64
40	(6.75)	2.55	40	(0.72)	(4.32)
60	(5.01)	2.57	60	(0.60)	(3.22)
80	(4.29)	2.41	80	(0.45)	(2.97)
100	(3.65)	(2.05)	100	(0.38)	(2.55)
150	(2.51)	(1.71)	150	(0.28)	(4.32)
200	(1.98)	(1.34)			

The radicals of *tert*-butyl peroxide likewise effect a dehydrogenation of the rubber.

Our results now make possible several additional quantitative statements with regard to the two reactions involved in thiuram vulcanization. It is possible, namely, to calculate their reaction velocity constants and their temperature dependence.

In Tables 1 through 3, the velocity constants of both the reaction of rubber with the three thiuram disulfides (k_{TD}) and that of the formation of the dithiocarbamic acid (k_{DC}) are plotted for the different temperatures. The numbers

TABLE 2

RATE CONSTANTS OF THE REACTION OF TETRAETHYLTHIURAM DISULFIDE WITH NATURAL RUBBER (k_{TD}) AND OF THE FORMATION OF THE DIETHYLDITHIOCARBAMATE (k_{DC})

120° C			130° C			140° C			150° C		
Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$	Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$	Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$	Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$
30	1.22	5.06	20	2.99	1.06	15	5.26	1.66	10	10.0	2.78
40	1.26	5.40	30	2.83	1.34	20	5.28	1.54	15	10.5	3.00
60	1.26	4.87	40	2.89	1.14	30	4.84	1.60	20	(8.60)	2.82
80	1.26	4.37	50	2.75	1.08	40	4.51	1.65	30	(7.74)	2.85
100	1.26	5.06	60	2.68	1.04	50	(4.03)	1.60	40	(6.27)	(2.36)
120	1.32	4.62	80	(2.44)	(0.98)	60	(3.53)	1.66	50	(5.23)	(2.25)
160	(1.09)	4.62	100	(2.14)	(0.89)	80	(3.11)	1.53	70	(4.08)	(2.04)
200	(0.92)	(3.99)	120	(1.95)	(0.87)	100	(2.70)	1.57	100	(2.99)	(2.16)
240	(0.80)	(3.92)	150	(1.60)	(0.82)	150	(1.91)	(1.21)	160	(2.17)	(1.89)
			200	(1.26)	(0.66)	200	(1.53)	(1.04)			

TABLE 3
RATE CONSTANTS OF THE REACTION OF TETRAPROPYLTHIURAM DISULFIDE
WITH NATURAL RUBBER (k_{TD}) AND OF THE FORMATION
OF DIPROPYLDITHIOCARBAMATE (k_{DC})

120° C			130° C			140° C		
Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$	Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$	Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$
30	1.30	(2.30)	20	2.28	(3.75)	20	(2.86)	(0.77)
60	1.19	3.64	30	2.29	5.67	40	3.66	1.15
100	1.04	3.79	50	1.93	6.93	60	3.83	1.11
150	0.95	3.62	75	(1.84)	7.11	80	3.43	1.10
200	0.83	3.48	100	(1.65)	6.50	100	(3.16)	1.07
250	(0.70)	(3.17)	125	(1.66)	6.04	125	(2.83)	0.99
300	(0.61)	(2.78)	150	(1.51)	5.76	150	(2.48)	(0.89)
400	(0.49)	(2.38)	200	(1.35)	(4.98)	200	(1.93)	(0.69)
700	(0.31)	(1.63)	350	(0.90)	(3.89)	—	—	—

150°			160° C		
Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$	Cure (min.)	$k_{TD} \cdot 10^3$	$k_{DC} \cdot 10^3$
10	(3.17)	(0.90)	10	(7.34)	3.67
15	6.27	1.64	15	14.40	3.82
20	8.07	2.63	20	17.40	3.68
30	9.25	2.63	30	12.70	3.65
40	7.67	2.40	45	9.33	(3.17)
60	5.89	2.05	60	(7.23)	(2.78)
80	(4.71)	1.81	90	—	(2.25)
100	(3.96)	1.63	150	—	(1.69)
180	(2.41)	(1.19)	—	—	—

given were calculated directly from the analytical results and not determined from the slope of the straight lines drawn through the points (see Figures 10 through 16 in part II). It thus becomes clear that one can actually speak of a constancy of the values obtained over a range of vulcanization times, which at times is a very extended one, so that it again becomes clear that the reactions involved here are of the first order. At the same time, however, it should be pointed out that, in every case and at every one of the temperatures chosen, there is observed a falling off of the reaction velocity constants above a certain vulcanization time. It is again seen that the relationships at lower temperatures

TABLE 4
SUMMARY OF THE MEAN VALUES OF THE RATE CONSTANTS

k min. ⁻¹	Temp. of cure (° C)	Tetramethyl- thiuram disulfide	Tetraethyl- thiuram disulfide	Tetrapropyl- thiuram disulfide
k_{TD}	87	1.44×10^{-3}	—	—
	120	2.97×10^{-3}	1.26×10^{-3}	1.06×10^{-3}
	130	5.07×10^{-3}	2.83×10^{-3}	2.17×10^{-3}
	140	9.50×10^{-3}	4.97×10^{-3}	3.64×10^{-3}
	150	1.62×10^{-1}	1.03×10^{-1}	7.43×10^{-3}
	160	—	—	1.34×10^{-1}
k_{DC}	87	6.48×10^{-4}	—	—
	120	1.03×10^{-3}	4.86×10^{-4}	3.63×10^{-3}
	130	1.57×10^{-3}	1.13×10^{-3}	6.34×10^{-3}
	140	2.57×10^{-3}	1.60×10^{-3}	1.08×10^{-2}
	150	4.64×10^{-3}	2.86×10^{-3}	2.11×10^{-2}
	160	—	—	3.71×10^{-2}

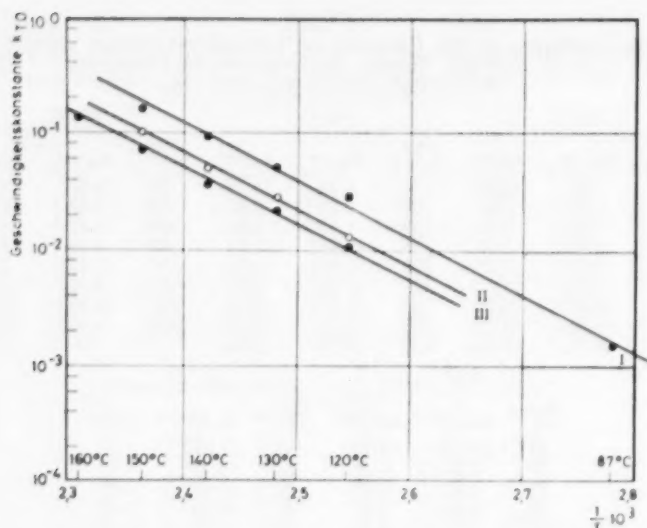


FIG. 1.—Dependence of the rate constants of the decrease of concentration of thioram disulfides in rubber on the temperature. I. Tetramethylthiuram disulfide. II. Tetraethylthiuram disulfide. III. Tetrapropylthiuram disulfide.

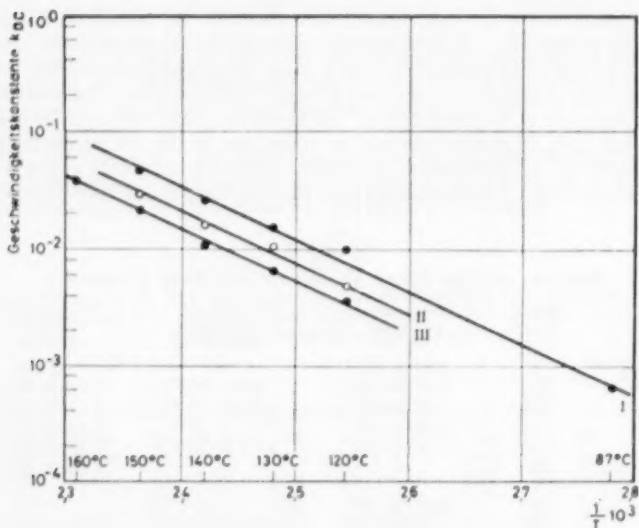


FIG. 2.—Dependence of the rate constants of the formation of dithiocarbamate on the temperature. I. Zinc dimethyldithiocarbamate. II. Zinc diethyldithiocarbamate. III. Zinc dipropyldithiocarbamate. The ordinate indicates the rate constant k_{pc} .

are the most definite. Finally, let it be noted that the velocity constants of the interaction of thiuram disulfides with rubber at each temperature are greater than those of the dithiocarbamate formation. We derived the average value of the reaction velocity constants for the several temperatures in every case from those values in Tables 1 through 3, which are not in parentheses. In this way the values given in Table 4 are obtained. If the logarithm of the reaction velocity constants is plotted against the reciprocal of the absolute temperature according to Equation 1, the relationships shown in Figures 1 and 2 result.

$$(1) \quad k = Ae^{-Q/RT} \longrightarrow \begin{array}{l} Q = \text{Activation energy} \\ A = \text{Frequency factor} \end{array}$$

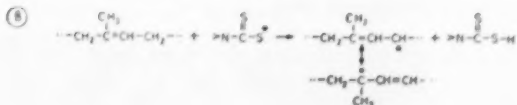
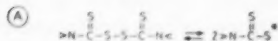
It is seen that both the constants, k_{TD} , of the reaction of rubber with thiuram disulfides and the splitting off of dithiocarbamic acid from the reaction product of thiuram disulfide and the allyl units of the rubber chain molecules, k_{DC} , are linear functions of the reciprocal of the absolute temperature, as required by the theory. We are led to regard this result especially as a confirmation of the reliability of our analytical study of thiuram vulcanization.

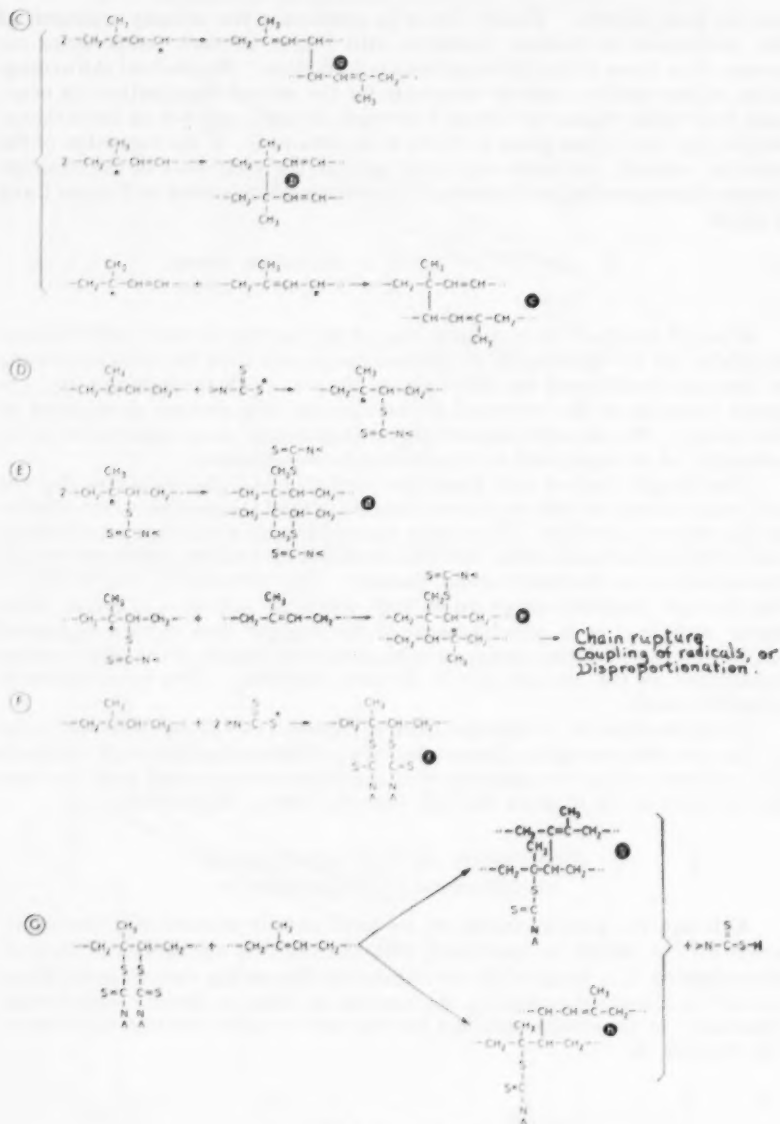
The straight lines of each figure are parallel, a fact that indicates that the activation energy of both reactions is independent of the particular constitution of the thiuram disulfide. This again proves that all three thiuram disulfides react with rubber and enter into the cross-linking reaction (dithiocarbamate formation) in an absolutely similar manner. The difference in constitution of the thiuram disulfides shows up in both reactions only in a different steric factor contained in A (displacement of the straight lines toward regions of smaller reaction velocity constants with increasing length of the alkyl portion substituted on the nitrogen in the thiuram disulfide). This is a completely plausible result.

From the slopes of the straight lines of Figures 1 and 2, the calculated value of the activation energy for the reaction of the thiuram disulfides with rubber is 22.7 calories and for the splitting off of the dithiocarbamic acid from the reaction product of the thiuram disulfide with the rubber, 20.4 calories.

DISCUSSION OF THE MECHANISM OF THIURAM VULCANIZATION

Although the kinetic studies, as we have already pointed out, cannot account for the details in connection with the reaction mechanism of thiuram vulcanization, it is worth while nevertheless to discuss the various possibilities. As will be shown immediately, the number of these is already considerably diminished by the results obtained (see the survey of the reaction mechanisms (A) through (G)).





Outline of reaction mechanisms

It may, for example, be assumed that thiuram disulfides enter into the reaction as radicals, for which we postulate an equilibrium according to (A). For this the dissociation of the thiuram disulfide can be hardly measurable, hence extremely slight. For the radicals, there are now two possibilities for

interaction with the allyl units of the rubber macromolecules. They can act on the allyl groupings at their α -methyl group. Concerning this group, it is known that it has a labile hydrogen and that it is capable of transferring this to other radicals, which then become saturated. Under these conditions we have a reaction according to (B). The polyisoprene chain radicals could combine intra- or intermolecularly (cross-linking), whereby there are, corresponding to scheme (C), three possibilities of coupling, which can lead to the configurations (a), (b), and (c). This mechanism would, to be sure, explain the complete interaction of the thiuram disulfide with the rubber, but not, however, its conversion to dithiocarbamate, which is independent of the temperature and amounts to only 66 per cent. Moreover, in case the process takes place according to (B) and (C), only a single reaction should be observed. That is, the decrease with time of the concentration of the thiuram disulfide during vulcanization ought to agree with the increase with time of the dithiocarbamate in the vulcanizate; that is, one would assume the reaction of the dithiocarbamic acid with zinc oxide to be what determines the velocity. This seems to be excluded. Thus one cannot attempt to explain the conversion of the thiuram disulfides, which always amount to 66 per cent, or better, their conversion into dithiocarbamate, which falls short of 100 per cent, by taking account of saturation of the polyisoprene chain radicals by radicals of the thiuram disulfide, even if this occurs to some extent. This is even without considering the fact that in such a case, the limiting value of the dithiocarbamate yield would certainly not be found to be independent of the temperature and of the chemical constitution. Furthermore, mechanisms (B) and (C) are not capable of explaining why the completely reacted and exhaustively extracted vulcanizates still contain sulfur.

The other possibility of the reaction of thiuram disulfides with the allyl units consists in their action on the double bonds. This can proceed in either of two ways. It can result in the complete saturation of a double bond, or in the attachment of only one thiuram radical to it. In the latter case, polyisoprene chain radicals are again created, and the reaction is comparable with the chain initiation of a polymerization induced by radicals.

If we consider the last type of reaction, then there is a mechanism according to (D). The chain radicals which then result can either react pairwise to give configuration (d), or according to a type of chain radical mechanism to give configuration (e). In the latter case, a chain termination reaction would probably occur after only a few steps. But even mechanisms (D) and (E) are not capable of accounting for the production of the dithiocarbamic acid and must, therefore, be given up for this particular reason as well as for the other ones. If the process were induced by reaction (D), it could, to be sure, account for the fact that all the thiuram disulfide reacts with the rubber. However, all the thiuram disulfide would then have to be firmly bound by the rubber. In other words, vulcanizates in the fully reacted state should contain an amount of sulfur corresponding to the original thiuram disulfide. This, however, is contrary to the facts. Finally, this mechanism, with regard to the dithiocarbamate formation, would require not two reactions, but only a single one.

Only when one considers a complete saturation of the double bonds by addition of thiuram disulfide radicals (mechanism (F)) does one arrive at a reaction path which can be brought into agreement with the relationships that have been found. The formation of adduct (f) first makes understandable the complete interaction of a thiuram disulfide with rubber and explains the con-

version of the thiuram disulfide as a "vulcanization-indifferent" reaction. We can properly assume with respect to this adduct that, in a further reaction, it acts more slowly with allyl units which are still unconverted, with splitting off of dithiocarbamic acid. This makes understandable the observation of two reactions. The reaction of adduct (f) according to (G) with still unconverted allyl units leads to the configuration (g) or (h). Their formulation corresponds to a 50 per cent conversion. However, the thiuram groups contained in them can again enter into reaction with the allyl units. It is, nevertheless, the further conversion of the groupings of type (g) and (h) which may be made more difficult and which could have as a consequence the failure of the conversion of the thiuram disulfide to the dithiocarbamate to attain 100 per cent.

It is clear that it is not yet possible to make any categoric final statement regarding the problem of the reaction mechanism of thiuram vulcanization. For this reason the above expositions merely represent ideas which can be entertained concerning it. Even if, on the basis of our experimental results, we are able to sketch an exact picture of thiuram vulcanization, we must, of course, nevertheless attempt to bring into the investigation the detailed insight into the constitution of the intermediate compounds and their reactivity with respect to allyl systems. This, however, can be carried out successfully only by a study of suitable model substances especially selected for the purpose.

SUMMARY

The present paper, which relates again to the problem of the kinetics of thiuram vulcanization, has led to the following results:

1. The velocity constants k_{TD} of the interaction of tetramethyl-, tetraethyl-, and tetrapropylthiuram disulfides with natural rubber, which proceeds according to a first-order reaction, are linear functions of the reciprocal of the absolute temperature. This is true also of the velocity constants k_{DC} of the dithiocarbamate formation.
 2. The activation energies of both reactions are independent of the particular chemical constitution of the thiuram disulfide involved.
 3. The different thiuram disulfides vary with respect to their reaction with rubber only by the steric factor.
 4. The reaction mechanism of thiuram vulcanization has been discussed in the light of the results of the kinetic investigation.
- These studies are being continued.

ACKNOWLEDGMENTS

During the course of our investigations of the vulcanization of rubber with thiuram disulfides, one of the authors (Scheele) has had repeated discussions on this problem with Professors H. Braune and F. Patat of the Technische Hochschule, Hannover. We are grateful to them for the lively interest that they have shown in our studies.

REFERENCES

- ¹ See preceding papers in this journal for Parts I and II.
- ² This is surprising in the formation of the dithiocarbamate, because the intermediate compound, from which the dithiocarbamate results, is formed in the course of vulcanization.
- ³ Farmer and Moore, *J. Chem. Soc.* 152, 142 (1951).

IV. INVESTIGATIONS WITH MODEL COMPOUNDS

WALTER SCHEELE AND OTTO LORENZ

INTRODUCTION AND STATEMENT OF THE PROBLEM

Our earlier investigations of the vulcanization of natural rubber with thiuram disulfides have contributed essentially to gaining an insight into the reactions involved¹. Above all they have shown that the concept, which appears over and over again in numerous publications², and according to which thiuram disulfides are split at vulcanization temperature into thiuram monosulfide and sulfur, and the cross-linking of the polyisoprene chains is produced by sulfur, can hardly be correct. Since the presence of thiuram monosulfide could not be demonstrated in any of the vulcanizates studied by us, but on the other hand, in the completely reacted vulcanizates there was in every case a considerable amount of zinc dithiocarbamate, an amount that was independent of the temperature and equal for all the homologous thiuram disulfides tested, namely 66 mole-per cent of the added thiuram disulfide, it seems more probable that the polyisoprene chains are joined together by C—C bonds. For this concept, one may suppose that the allyl groups of the polyisoprene finally undergo dehydrogenation and that dithiocarbamic acid is formed, which combines to give zinc dithiocarbamate. In this light the conversion of thiuram disulfides in rubber has many parallels with the reaction of benzoyl peroxide and of di-*tert*-butyl peroxide with natural rubber as well as with model compounds like cyclohexene, 1-methyl-cyclohexene, 4-methyl-heptene, etc.³. Here too the essential process is a dehydrogenation of these compounds by the peroxides. This results in a linking of the radicals formed by C—C linking in which, to be sure, there occurs in every case a mixture of the theoretically possible compounds ("polymers"). This mixture can, in some cases, be separated into definite compounds.

We do not, however, wish to deny the possibility of the reactions of thiuram disulfides which are frequently put forward in connection with discussions of the mechanism of the vulcanization of rubber with thiuram disulfides, namely their thermal splitting into thiuram monosulfide and sulfur, followed by further splitting into tetraalkylthiourea and carbon disulfide. Yet they must presumably take place much more slowly than the conversion of the thiuram disulfide with rubber and thus elude observation.

Our study of the kinetics of the vulcanization of natural rubber with thiuram disulfides at a series of temperatures indicated that apparently two reactions are involved, namely, a relatively rapidly occurring interaction of the thiuram disulfides with the rubber, which results in the formation of a "preliminary stage of vulcanization", and the more slowly occurring vulcanization, which is accompanied by the formation of zinc dithiocarbamate. Both reactions are of the first order up to a conversion considerably in excess of 50 per cent at higher temperatures and over the whole range as well at temperatures below 100° C. From the temperature dependence of their velocity constants, their energies of activation can be calculated.

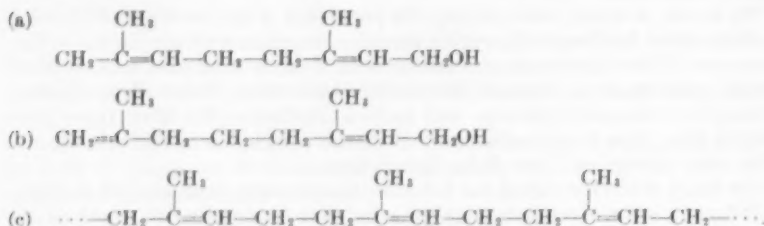
That it was possible to throw light on the kinetic relationships in thiuram vulcanization may properly be regarded as a confirmation of the reliability of the conductometric titration method used by us⁴, and it also argues the correctness of our methodical procedure, whose first step is characterized by the systematic study of the material conversions during vulcanization reactions

with the aid of quantitative chemical analyses. Now it is of great importance for understanding the cross-linking of rubber by thiuram disulfides that one be able to form a mental picture of the constitution of the cross-linking points. In this way, one is enabled occasionally to calculate the number of cross-linking positions per mole of thiuram disulfide converted, and could perhaps test many theoretical formulations of the dependence of a series of properties of the rubber on the degree of vulcanization.

For this purpose, however, it is necessary to broaden the studies to include model compounds. Before one can direct his efforts in that direction, however, it is necessary to test whether thiuram disulfides react with such compounds in exactly the same manner as with natural rubber. If, in fact, an unambiguous reaction takes place between the allyl groups of the polyisoprene chains and the thiuram disulfides, as seems probable according to our experimental results, then one must expect that model compounds of lower molecular weight, which contain some allyl groupings of the same constitution and interconnections as in rubber (for example, dihydromyrcene, geraniol, squalene, etc.), would react with thiuram disulfides in exactly the same way as rubber does. Indeed, the same relationships should be found quantitatively, as in the vulcanization of rubber with thiuram disulfides.

The present paper deals with studies of the reaction of tetraethylthiuram disulfide with geraniol, in xylene as solvent, in the presence of zinc oxide. The same procedure was followed as previously in the case of the interactions between thiuram disulfides and rubber.

Geraniol is a pleasant smelling liquid which is contained in the oil of roses in amounts of 40-60 per cent. It contains a mixture of two isomeric *trans*-alcohols (a) and (b), with two allyl groups in the molecule⁴. The configuration (a), for example, can be considered as a segment out of the polyisoprene chain (c), one end of which is terminated by a hydrogen atom, while the other ends in a hydroxyl group.



EXPERIMENTAL

The reaction vessel was a round-bottom flask with numerous side tubes, equipped with a stirrer cooler, with tubes to introduce a gas stream, to receive a thermometer, and to remove samples. It was placed in a thermostat, which was brought to the proper temperature to give the desired temperature in the flask for each experimental run. At the start of each experiment the flask was charged with a measured amount of xylene solution of known content of the purest geraniol. Then an exactly weighed amount of zinc oxide was added. As soon as the solution had reached constant temperature, a measured volume of a solution of known content of tetraethylthiuram disulfide in xylene was added, and the time of the start of reaction noted. The solution was stirred vigorously

and continuously, and both for several hours before the reaction and during it, a stream either of pure nitrogen or of air was passed through the solution. From time to time samples were removed, cooled as quickly as possible, and prepared for analysis. In all the experiments, the geraniol was present in large excess (see Table 1).

It proved necessary, in order to remove any finely divided zinc oxide, to filter each sample through a membrane filter. Otherwise even the most minute amounts of zinc oxide remaining in the solutions introduce slight errors in the analytical values for the zinc dithiocarbamate⁶. After thus removing the zinc oxide from the solution, the xylene was distilled off in vacuum. A solution of zinc dithiocarbamate remains and any still unconverted thiuram disulfide in geraniol, which also still contains the reaction product of the geraniol with thiuram disulfide. It was taken up in the purest acetone and brought to a definite volume in a measuring flask. Portions thereof were introduced into a conductivity cell, diluted with water and analyzed quantitatively for dithiocarbamate and thiuram disulfide. The zinc dithiocarbamate was determined

TABLE I

DECREASE OF THIURAM AND INCREASE OF DITHIOCARBAMATE IN THE REACTION OF GERANIOL WITH TETRAETHYLTHIURAM DISULFIDE UNDER NITROGEN

The reaction mixture was made up of: tetraethylthiuram disulfide, 900 mg.; zinc oxide, 3 g.; geraniol, 20 cc.; and xylene, 800 cc.

137° C			122.5° C			110° C			100° C		
Time (min.)	Mol.-% thiuram	Mol.-% dithiocarbamate	Time (min.)	Mol.-% thiuram	Mol.-% dithiocarbamate	Time (min.)	Mol.-% thiuram	Mol.-% dithiocarbamate	Time (min.)	Mol.-% thiuram	Mol.-% dithiocarbamate
10	69.7	13.5	15	88.6	5.5	90	71.6	14.3	120	85.2	6.1
20	47.9	25.6	30	74.6	10.3	180	52.1	24.5	240	67.8	12.0
30	35.3	32.9	45	63.2	14.8	270	33.2	33.7	360	56.4	18.6
40	26.5	41.3	60	54.3	20.0	360	22.6	43.1	540	42.3	25.5
60	12.8	51.4	90	38.8	28.2	480	14.5	50.0	720	31.8	30.8
90	5.9	58.2	120	25.8	35.9	600	7.3	55.8	900	23.3	36.9
120	2.5	64.0	180	12.7	46.4	840	—	61.4	1440	10.0	48.3
180	—	66.1	240	8.1	55.5	1380	—	65.8	1800	5.5	52.0
240	—	66.7	360	—	59.2	1800	—	67.1	2220	—	(51.7)
300	—	67.2	—	—	—	—	—	—	2880	—	(51.4)

by conductometric titration with hydrochloric acid of known strength, and the thiuram disulfide then determined by conductometric titration with copper sulfate solution, with the addition of hydroquinone. It is not necessary here to remove the excess geraniol which is still present, nor is it necessary, as the experimental results will show, to assume that the reaction product of the geraniol influences the analytical results.

EXPERIMENTAL RESULTS AND DISCUSSION

THE INTERACTION OF TETRAETHYLTHIURAM DISULFIDE WITH GERANIOL UNDER NITROGEN

Although we convinced ourselves by control tests that zinc dithiocarbamate experiences no change even after being heated in xylene for sixteen hours under the influence of either air or nitrogen, we carried out all our studies at first with painstaking exclusion of oxygen. To this end a stream of pure nitrogen was passed through the solution of the reaction partners⁷. The results obtained in these experimental tests are collected in Table I. This gives the increase of the concentration of the zinc dithiocarbamate, as well as the decrease of the thiuram disulfide for different temperatures.

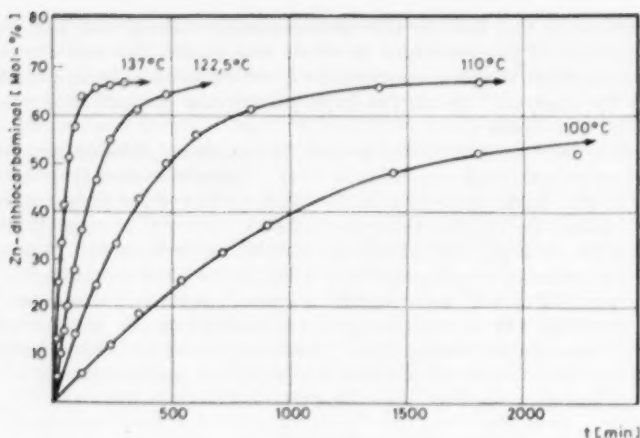


Fig. 1.—Increase of concentration of zinc diethyldithiocarbamate with reaction time in the interaction of tetraethylthiuram disulfide with geraniol.

Figure 1 shows the rise of the concentration of zinc dithiocarbamate in the solution with the reaction time. Figure 2, in which the ordinate is the logarithm of the zinc dithiocarbamate yield in mole-per cent of the initial thiuram disulfide and the abscissa is the reciprocal of the reaction time $1/t \cdot 10^3$, shows that, similarly in the conversion of thiuram disulfide with geraniol, the amount of zinc dithiocarbamate formed at infinite reaction times is independent of the temperature and has the limiting value of 66 mole-per cent calculated on the

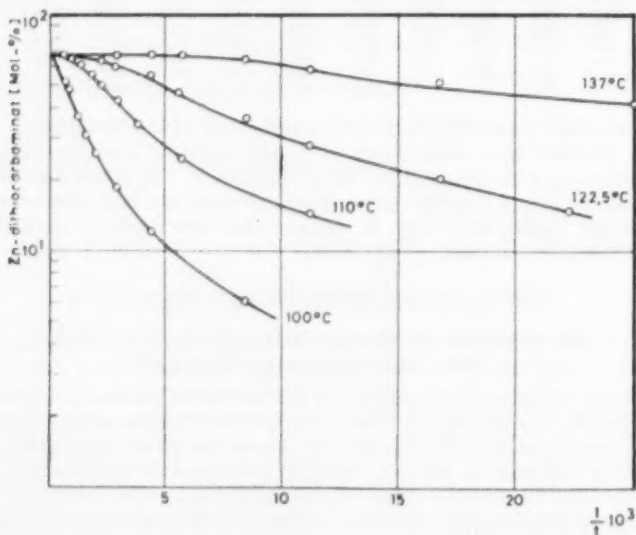


Fig. 2.—Demonstration of the final value of the yield of diethyldithiocarbamate in the interaction of tetraethylthiuram disulfide with geraniol in nitrogen.

initial amount of thiuram disulfide present. Thus the same relationships exist as in the vulcanization of natural rubber with thiuram disulfides.

In the above case we have been able to convince ourselves that the limiting value of the dithiocarbamate yield is also independent of the concentration of the added thiuram disulfide. Although it is not specifically demonstrated here, we found, namely, that even when the amount of thiuram disulfide caused to react was doubled or quadrupled or reduced to one-half of the usual normally added amount, the limiting value of zinc dithiocarbamate was 66 mole-per cent.

In our recent publication we attempted to explain the invariable 66 mole-per cent conversion of thiuram disulfide to the dithiocarbamate which occurs in the vulcanization of natural rubber by postulating that the vulcanization reaction, which is accompanied by the formation of dithiocarbamate, is hindered by the increase of the number of points of cross-linking and, therefore, also

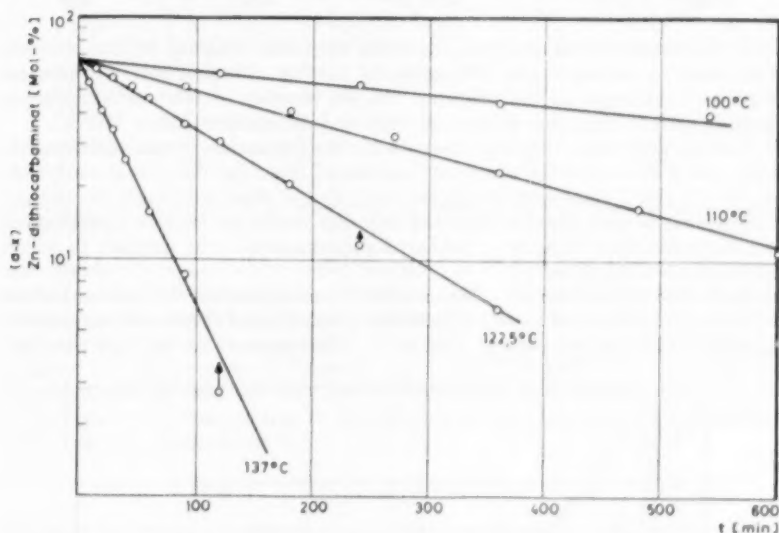


FIG. 3.—Variation of the concentration of zinc diethyldithiocarbamate as a first-order reaction.

fails to run to completion. But after it turned out that the same limiting value of the dithiocarbamate yield is also reached in the interaction of the thiuram disulfide with geraniol, which takes place in the homogeneous liquid phase, and here too the value is independent of the concentration, as can also be assumed in the vulcanization of rubber, we can no longer support this interpretation (given in the second communication of this series). On the same basis the interpretation of Jarrijo, which is not unlike ours, presumably does not really hit the mark either. It now seems much more probable to us that the temperature-independent limiting value of the molar conversion of the thiuram disulfide to the dithiocarbamate, as it is effected by the natural rubber or the geraniol, is the result of a stoichiometric reaction.

From Figure 3 it can be seen that the reaction of tetraethylthiuram disulfide with geraniol is a first-order reaction with respect to the formation of dithiocarbamate, and it is clear that this is true in this case for all the reaction

TABLE 2
REACTION VELOCITY CONSTANTS OF INCREASE OF DITHIOCARBAMATE
(Interaction of Tetraethylthiuram Disulfide with Geraniol in a Stream of Nitrogen)

137° C		122.5° C		110° C		100° C	
Time (min.)	$k_{pc} \cdot 10^3$ min. ⁻¹	Time (min.)	$k_{pc} \cdot 10^3$ min. ⁻¹	Time (min.)	$k_{pc} \cdot 10^3$ min. ⁻¹	Time (min.)	$k_{pc} \cdot 10^3$ min. ⁻¹
10	2.23	15	5.74	90	2.65	120	7.93
20	2.42	30	5.55	180	2.54	240	8.26
30	2.26	45	5.60	270	2.64	360	9.10
40	2.41	60	5.90	360	2.88	540	8.94
60	2.45	90	6.08	480	2.88	720	8.62
90	2.28	120	6.40	600	3.01	900	8.95
120	2.67	180	6.59	840	3.01	1440	8.93
	—	240	7.35	1380	3.04	1800	8.44
Mean	2.39		6.15		2.83		8.64

times and temperatures observed, for in the very fluid medium (xylene solution of the reaction partners) and with constant stirring, diffusion has, of course, no longer any influence on the reaction. In the reaction of tetramethylthiuram disulfide with rubber, this is the case only at temperatures below 100° C.

Table 2 gives the velocity constants for the formation of zinc dithiocarbamate. It is seen that the constants calculated from the individual analytical results of Table 1 show excellent agreement, that is, show only slight deviations. They are somewhat greater than the velocity constants for the formation of zinc diethyldithiocarbamate in rubber, a consequence of the medium in which the reaction takes place.

As it does in the thiuram vulcanization of natural rubber, the concentration of the disulfide drops off to zero also in the interaction of thiuram disulfide with geraniol. This can be seen in Figure 4. The decrease of thiuram disulfide

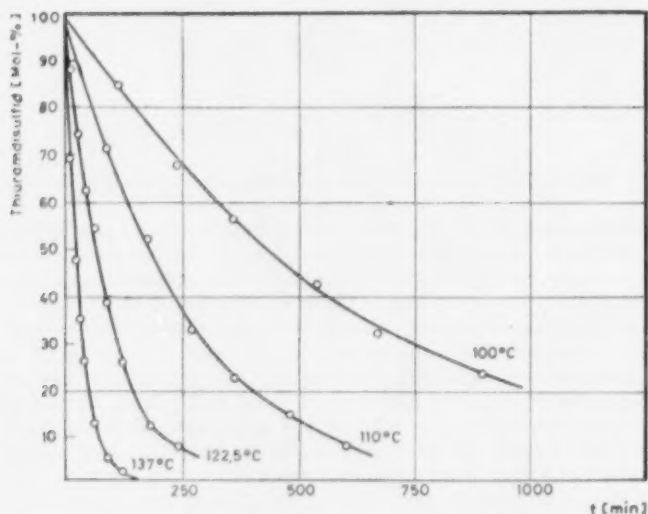


FIG. 4.—Decrease of the concentration of tetraethylthiuram disulfide with the duration of the reaction with geraniol.

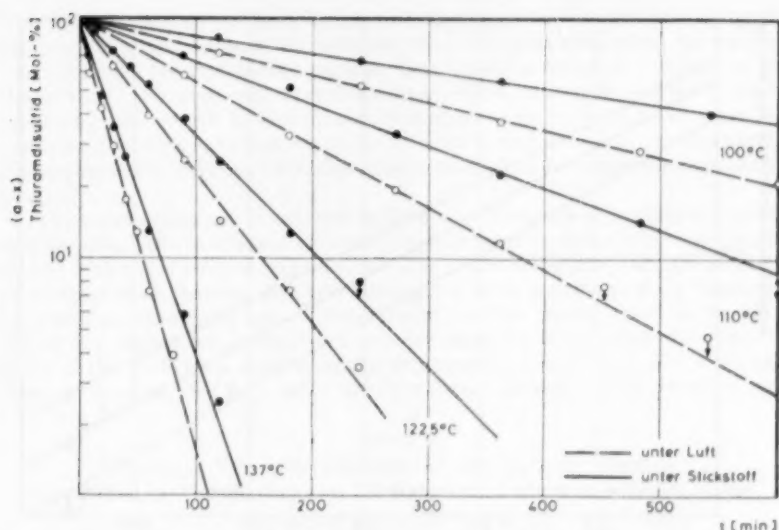


Fig. 5.—Decrease of concentration of tetraethylthiuram disulfide in the reaction with geraniol is a first-order reaction. The solid lines represent the reaction in nitrogen; the broken lines the reaction in air.

concentration is again a first-order reaction, as Figure 5 shows (see the solid curves). The ordinates give the logarithm of the amount of thiuram disulfide in mole-per cent present at any time, the abscissa the reaction time in minutes. The velocity constants, calculated from the coordinates of the individual points of the solid curves of Figure 5, are collected in Table 3. These too are somewhat greater than the ones for the interaction with rubber.

In Figure 6, corresponding to the relation for the temperature dependence of the reaction velocity constants:

$$k = A \cdot e^{-Q/RT} \quad Q = \text{activation energy}$$

the log of the velocity constants k_{TD} of the decrease of thiuram, and k_{DC} of the increase of dithiocarbamate (curves 1 and 2) is plotted as a function of the

TABLE 3
REACTION VELOCITY CONSTANTS OF DECREASE OF THIURAM (INTERACTION OF TETRAETHYLTHIURAM DISULFIDE WITH GERANIOL IN A STREAM OF NITROGEN)

137° C		122.5° C		110° C		100° C	
Time (min.)	$k_{TD} \cdot 10^3$ min. ⁻¹	Time (min.)	$k_{TD} \cdot 10^3$ min. ⁻¹	Time (min.)	$k_{TD} \cdot 10^3$ min. ⁻¹	Time (min.)	$k_{TD} \cdot 10^3$ min. ⁻¹
10	3.77	15	8.15	90	3.70	120	1.34
20	3.68	30	9.75	180	3.62	240	1.62
30	3.48	45	10.17	270	4.08	360	1.57
40	3.32	60	10.15	360	4.12	540	1.58
60	3.41	90	10.47	480	4.02	720	1.59
90	3.14	120	11.25	600	4.35	900	1.62
120	3.14	180	11.43	—	—	1440	1.60
—	—	240	10.48	—	—	1800	1.61
Mean	3.42		10.23		3.98		1.57

zinc dithiocarbamate in the solution was arrested prematurely, that is, before attaining the final value of 66 mole-per cent, and that even when the process was observed for still longer periods, the dithiocarbamate concentration no longer rose. We supposed that these unexpected relationships were possibly caused by the oxygen in the air and that when samples were taken from the reactions flasks perhaps this was introduced now and then into the solution in slight quantities. At any rate, this observation led us to repeat the tests under air.

The results obtained are shown in Table 4. From these analytical results, it is seen that the thiuram disulfide again falls to zero, and, by comparing the figures with the corresponding ones in Table 1, it is recognized that the reaction of geraniol with thiuram disulfide takes place more rapidly in the presence of oxygen than under nitrogen. Nevertheless, as the dashed curve in Figure 5 shows, the conversion is again a first-order reaction, except that the negative slope of the curves are steeper in the experiments under atmospheric oxygen than in those carried out under nitrogen (solid curves). The velocity con-

TABLE 5
REACTION VELOCITY CONSTANTS OF DECREASE OF THIURAM
(Interaction of Tetraethylthiuram Disulfide with Geraniol in a Stream of Air)

137° C		122.5° C		100° C		100° C	
Time (min.)	$k_{TD} \cdot 10^3$ min. ⁻¹	Time (min.)	$k_{TD} \cdot 10^3$ min. ⁻¹	Time (min.)	$k_{TD} \cdot 10^3$ min. ⁻¹	Time (min.)	$k_{TD} \cdot 10^3$ min. ⁻¹
10	5.20	30	1.50	90	5.88	120	2.54
20	4.17	60	1.52	180	6.17	240	2.61
30	4.14	90	1.49	270	6.01	360	2.69
40	4.37	120	1.60	360	6.02	480	2.56
50	4.12	180	1.45	450	5.67	600	2.47
60	4.40	240	1.35	540	5.65	720	2.38
80	4.05	—	—	—	—	840	2.38
	—	—	—	—	—	1380	2.23
Mean	4.35		1.48		5.90		2.48

stants, calculated from the experimental results, are given in Table 5. The especially good agreement of the values for the constants are evidence of the exactness of the measurements.

From the temperature dependence of the velocity constants (curve 3 of Figure 6), there is calculated a somewhat smaller energy of activation. We find $Q_{TD} = 23$ cal. for the interaction of thiuram disulfide with geraniol under air, compared with $Q_{TD} = 25$ cal. under nitrogen.

More remarkable even than the altered relationships of the thiuram disulfide reaction is what happens with respect to the increase of the concentration of zinc dithiocarbamate during the reaction. In none of the series of experiments is the limiting value of 66 mole-per cent reached in the yield of dithiocarbamate. The completely reacted mixtures in all cases contain less zinc dithiocarbamate than the expected amount, and less and less, the lower the temperature. Whether at still higher temperatures than the highest used, the 66 mole-per cent limiting value of zinc dithiocarbamate would eventually be reached, and whether at lower temperatures there would be eventually a smaller limiting value, which no longer changed when the reaction temperature is lowered still more, was not investigated at this time. In any case, we are led by the temperature dependence of the limiting value of the conversion

under the influence of atmospheric oxygen, which is evident in Figure 7, to conclude that the thiuram disulfide is involved, because of the presence of oxygen, in another additional reaction in which no dithiocarbamate is formed. It seems to us certain that the atmospheric oxygen also has an influence on the thiuram vulcanization. At the outset of our studies of the mechanism of vulcanization, we vulcanized sheets of rubber in a drying oven with thiuram disulfide, and we observed that varying and uncontrollable limiting values of zinc dithiocarbamate were reached. These values were always less than 66 mole-per cent, an effect, without question, of the influence of atmospheric oxygen. For this reason, however, one must also assume that in vulcanization

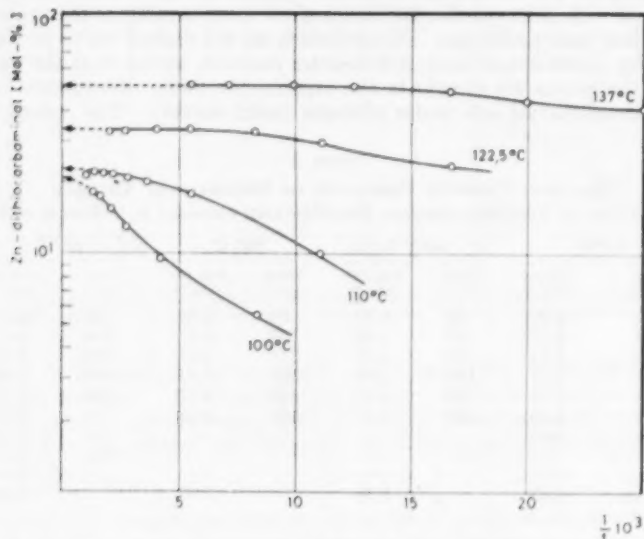


Fig. 7.—Demonstration of the dependence on temperature of the limiting value of the yield of zinc diethyldithiocarbamate in the interaction of tetraethylthiuram disulfide with geraniol in air.

in closed molds there is no oxygen present, otherwise one could not explain why, in the reaction of thiuram disulfide with geraniol under nitrogen, 66 mole-per cent of thiuram disulfide is consistently converted to dithiocarbamate.

The relationships noted above should also be taken into consideration when it is attempted to prepare the reaction product or products from thiuram disulfide and geraniol. It is certainly recommended that the conversion itself should be allowed to take place under nitrogen, otherwise it is likely that more complex and constantly changing products will be formed. In general it is not possible in any case to predict the detailed behavior.

CONCLUSIONS AND SUMMARY OF THE RESULTS

If we disregard for the moment the phenomena which occur in the interaction of thiuram disulfide with geraniol under the influence of air and confine our consideration to the results which can be deduced from the study of this reaction in a stream of nitrogen, we are led to the conclusion that geraniol,

which was used as a model compound, behaves with respect to its interaction with tetraethylthiuram disulfide, not only qualitatively but also quantitatively, exactly like rubber, and that it is not to be assumed that other tetraalkylthiuram disulfides as well as other compounds which are analogous to geraniol will behave differently. Thus the results can be evaluated as a proof that the vulcanization of natural rubber by thiuram disulfides depends on nothing other than a definite and always similar interaction with the allyl groups of the polyisoprene chain. The results of the investigation described in this paper can be regarded, moreover, as support for the correctness of our procedure in the clarification of the vulcanization mechanisms, and they stress the importance of analytical-chemical methods, which have certainly not been pursued in the past with the necessary intensity and insight.

These investigations are being continued. It has already been found that the vulcanization of natural rubber with thiuram monosulfides and sulfur leads to the same results as vulcanization with thiuram disulfides. This has been conjectured, to be sure, by a number of workers. However, it was never really demonstrated experimentally. We shall report on this in the near future.

The experimental results can now be summarized as follows:

1. The reaction between thiuram disulfide and geraniol (demonstrated by the example of tetraethylthiuram disulfide) takes place qualitatively and quantitatively like the interaction between thiuram disulfide and natural rubber. In the vulcanization of rubber by thiuram disulfides, therefore, there is involved a reaction of the thiuram disulfide with the allyl groups, leading to a definite conversion.

2. It was found that in the interaction of geraniol with thiuram disulfide under nitrogen and in the presence of zinc oxide, the limiting value of zinc dithiocarbamate amounts to 66 mole-per cent of the original thiuram disulfide, independent of the temperature. This was the result found in the study of the reaction of the thiuram disulfides with rubber.

3. We were able to show that the limiting value of the dithiocarbamate yield in the interaction of tetraethylthiuram disulfide with geraniol is independent of the thiuram disulfide concentration. This is likewise true for the reaction of the thiuram disulfides with natural rubber. From this it follows that the interaction of thiuram disulfides with allyl groupings, as they occur in the polyisoprene chain, is apparently a stoichiometric one. For this reason we can no longer retain the assumption that the limiting value of the yield of dithiocarbamate is the result of a sterically hindered reaction.

4. The change of concentration of zinc dithiocarbamate in the interaction of tetraethylthiuram disulfide with geraniol under nitrogen can be accounted for by postulating a reaction of the first order. The velocity constants were calculated and it was found that the resulting activation energy is somewhat greater than the one for the interaction with natural rubber.

5. Similarly the concentration of thiuram disulfide obeys a first-order reaction as it falls off to zero. The velocity constants were calculated. The activation energy obtained from the temperature dependence is in good agreement with that found for the interaction with rubber.

6. In the presence of oxygen, the reaction between thiuram disulfide and geraniol takes a quite different course. The rate of decrease of concentration of thiuram disulfide, which likewise follows a first-order reaction, is higher. The yield of zinc dithiocarbamate does not attain the constant value of 66 mole-per cent of the original thiuram disulfide. In the temperature range studied,

the amount of dithiocarbamate found is smaller. The limiting value reached at the various temperatures is progressively smaller, the lower the temperature chosen. Whether by expanding the temperature range, one would eventually reach a minimum and a maximum limiting value has not been investigated.

ACKNOWLEDGMENT

This work has been carried out with the support of the Kautschukzentral-forschungslaboratorium of the Bayer A. G. Dye Works in Leverkusen. We are indebted to the Director, Dr. E. Konrad, for furnishing us with chemicals and solvents. We also owe our thanks to Mr. Gerberding (Fa. Dragoco, Holz-minden) for supplying us gratis with geraniol.

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- ¹ Scheele, Lorenz, and Dummer, *Kautschuk u. Gummi* **7**, WT 273 (1954); **8**, WT 2 and 27 (1955); this issue *RUBBER CHEM. & TECHNOL.*
- ² See the comprehensive presentation of our knowledge of the vulcanization of rubber by Farmer in "Advances in Colloidal Science", Vol. II, Rubber, 347 ff. This treatise contains further literature references to this problem. Similarly in more recent publications (Craig *et al.*, *J. Polymer Sci.* **5**, 709 (1950); **6**, 1, 13, 177 (1951); **8**, 321 (1952)), there appears again invariably the same confusion that prevails in the question of the reaction mechanism of thiuram vulcanization, with and without the presence of sulfur. One gets the impression there that even vulcanization of rubber by thiuram disulfide in the absence of sulfur is regarded as a sulfur vulcanization, although at times the possibility of the formation of C—C cross-linking bridges is discussed (see also Flory, "Principles of Polymer Science", New York, 1952, p. 456).
- ³ Farmer and Moore, *J. Am. Chem. Soc.* **73**, 131, 142 (1951). Van Rossem, in his studies with benzoyl peroxide, also arrives at the result of a cross-linking of the chain molecules of rubber by C—C bonding. (Cited by Fisher, *Ind. Eng. Chem.* **31**, 1361 (1939).) See also Farmer and Michael, *RUBBER CHEM. & TECHNOL.* **16**, 465 (1943).
- ⁴ The procedure previously developed by us was published in this journal: Scheele and Gensch, *Kautschuk u. Gummi* **6**, WT 147 (1953); **7**, WT 122 (1954); Scheele and Gensch, *Kautschuk u. Gummi* **8**, WT 55 (1955); this issue *RUBBER CHEM. & TECHNOL.*
- ⁵ Fieser and Fieser, "Lehrbuch der organischen Chemie", Verlag Chemie GmbH, Bergstrasse, Weinheim, 1954, p. 1118.
- ⁶ This could be clearly seen from the characteristics of the curves of conductometric titration.
- ⁷ If a corresponding control test with thiuram disulfide is performed, one observes a very slow formation of zinc dithiocarbamate. It should be stressed that this reaction certainly proceeds far more slowly than the interaction of thiuram disulfide with geraniol in xylene. The result is the same, however, whether the experiment is carried out with exposure to atmospheric oxygen or under nitrogen.
- ⁸ Jarrijo, *RUBBER CHEM. & TECHNOL.* **19**, 1061 (1946). In this author's opinion, thiuram disulfides did indeed effect a C—C linking, but he claimed that a constant limiting value of dithiocarbamate yield is the result of a "statistical" reaction mechanism. Jarrijo attempted to support this concept by developing a corresponding reaction scheme.

V. VULCANIZATION OF NATURAL RUBBER BY TETRAMETHYLTHIURAM MONOSULFIDE AND SULFUR

WALTER SCHEELE AND GEORG BIELSTEIN

STATEMENT OF THE PROBLEM

In a recent publication¹ we showed that thiuram disulfides react with geraniol, $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2\text{OH}$, in the absence of oxygen not only qualitatively, but also quantitatively, as they do with natural rubber². Independent of the temperature, 66 mole-per cent of the original thiuram disulfide was again converted to the corresponding dithiocarbamic acid, and this combines with zinc oxide to form zinc dithiocarbamate, which is stable under the conditions of vulcanization. Over the whole range of reaction times studied, both the decrease of concentration of the thiuram disulfide and the formation of the zinc dithiocarbamate proved to be reactions of the first order. The first of the two is the more rapid one.

With these results it was possible for the first time to show in a convincing manner that it is reasonable and worthwhile in investigations of vulcanization processes to make comparative studies of corresponding transformations employing lower molecular model compounds. It can be concluded in this case that the vulcanization of natural rubber by thiuram disulfides depends without question, and exclusively, on their interaction with the 1,5-diene units of the macromolecules, and therefore it must also be possible to obtain information about the constitution of the cross-linking points, by attempting to prepare the reaction products of lower molecular 1,5-dienes with thiuram disulfides, and to throw light on their constitution. It is advisable here to work under mild experimental conditions and to take the utmost care to exclude oxygen, for, under the influence of oxygen, as we have likewise shown, the conversion takes a different course. Such studies are to be undertaken by us.

The results of our studies up to this time make it probable that thiuram disulfides cause a linking of the macromolecules of polyisoprene through C—C bonds. In any case, in our opinion, one cannot assume that thiuram disulfides under vulcanization conditions go over into thiuram monosulfide and sulfur and that the sulfur is the actual vulcanizing agent. This is a concept that one finds again and again in the literature on this subject³. At no stage of the vulcanization and at none of the vulcanization temperatures selected could thiuram monosulfide be detected, a fact already noted by Jarrijon⁴. This, however, leads naturally to the supposition that vulcanization of natural rubber by thiuram monosulfide and sulfur is nothing else than vulcanization by thiuram disulfide formed under vulcanization conditions.

The present paper deals with the results obtained in the vulcanization of natural rubber by tetramethylthiuram monosulfide and sulfur. The proportions were so chosen that there was 1 gram-atom of sulfur per mole of thiuram monosulfide. All experiments were carried out in the presence of an excess of zinc oxide.

EXPERIMENTAL

The starting material used in the course of the present investigation, as previously, was pale crepe, which was exhaustively extracted with acetone in a Soxhlet apparatus. After sufficient mastication at about 60° C (no attempt was made to reach a definite degree of mastication), there was added to a weighed amount of the masticated rubber first zinc oxide, then tetramethylthiuram monosulfide, and finally sulfur. All were weighed accurately. The mixing of the added ingredients on the mill rolls was continued until visual inspection indicated that a completely homogeneous mass had formed. Portions of the material so prepared were vulcanized in suitable molds to give round disks about 3 mm. thick and from 70 to 80 mm. in diameter.

Vulcanization itself was carried out in a thermostat. The heating fluid was Clophen A-30. The molds were closed tightly by means of a press and then placed either singly, or in experiments involving longer vulcanization times, in a stack of six in the thermostat, which was previously heated to the particular desired temperature. After definite and always accurately measured vulcanization periods, they were taken out and rapidly cooled to room temperature with cold water. At room temperature, vulcanization comes practically to a standstill.

A vulcanizate prepared in this manner was cut up into small pieces, and an exactly weighed amount extracted for at least four days at room temperature with the purest ethyl acetate. The extracting liquid was renewed several

times during the extraction. The extracts were collected in a measuring flask filled to a definite volume with ethyl acetate. In the solutions obtained in this way, the zinc dithiocarbamate formed in the vulcanization was determined quantitatively by conductometric titration with hydrochloric acid⁶.

For this purpose a measured volume of the solution was introduced into a conductivity cell, provided with a ground-glass joint and tube, so that the ethyl acetate could be vacuum distilled off. The residue after distillation was dissolved in acetone and the acetone solution diluted with water just to a point short of producing precipitation. Then the conductometric titration was carried out with the conductivity cell in a thermostat at 45° C. This quantitative determination of the dithiocarbamate is not influenced adversely by either sulfur or thiuram monosulfide.

EXPERIMENTAL RESULTS

QUALITATIVE OBSERVATIONS

If one examines the ethyl acetate extracts of a series of vulcanizates of increasing times of vulcanization, one notes that their yellow color is more intense and brilliant than that of extracts of corresponding thiuram disulfide vulcanizates. From this it should probably be concluded that vulcanizates obtained with thiuram monosulfide and sulfur will show free thiuram monosulfide. But one also notes that the color of the extracts from the vulcanizates of short reaction times all the way to practically exhaustively reacted vulcanizates becomes less and less intense. The latter have the pale yellow color that we have always observed in the extracts of thiuram disulfide vulcanizates, a color also shown by the acetone extracts of pale crepe. For this reason, however, it can now be supposed that the thiuram monosulfide disappears progressively during the vulcanization, and the simplest assumption is that it goes over into thiuram disulfide by combining with the sulfur. However, it was found that all vulcanizates contain practically no thiuram disulfide, so that, in any case, this can be present in only negligible amount. To understand this, let us remember that warm solutions of thiuram disulfide in water plus acetone quickly give a precipitate of copper dithiocarbamate on the addition of copper sulfate and hydroquinone, whereas solutions of thiuram monosulfide under the same conditions give a dark brown precipitate that forms only very slowly. Now if, in the above case, one treats the extracts of the vulcanizates in a water and acetone solution with copper sulfate and hydroquinone, after first destroying with acid the dithiocarbamate, which again forms in considerable amount, there develops only after a rather long time a brown precipitate. This is doubtless a result of thiuram monosulfide that is still present. Thus the additional supposition can be made that the thiuram disulfide, insofar as it is formed under the conditions of vulcanization, and it must be, is immediately used up by the rubber.

Thus, in order to obtain a complete understanding of this vulcanization reaction, one should follow by measurement two processes: (1) the decrease with time of the concentration of the thiuram monosulfide and of the sulfur in the vulcanizate, presumably a bimolecular reaction, and (2) the increase with time of the concentration of the zinc dithiocarbamate. In the following exposition we deal first with the formation of the zinc dithiocarbamate, since the results which were obtained in this connection already make it possible to recognize what is the essential feature in the vulcanization of natural rubber with thiuram monosulfide and sulfur.

QUANTITATIVE RESULTS

The vulcanization of natural rubber with tetramethylthiuram monosulfide and sulfur (1 gram-atom sulfur per mole of thiuram monosulfide) was carried out at 150°, 140°, 130°, 120°, 110°, 100°, and 90° C. The amounts of zinc dithiocarbamate found in the vulcanizates prepared at these temperatures and at each temperature at a series of times of vulcanization, are given in Table 1, expressed in mole-per cent of the initial thiuram monosulfide.

TABLE 1

RESULTS OF THE QUANTITATIVE ANALYSES OF ZINC DITHIOCARBAMATE IN EXTRACTS OF DIFFERENT VULCANIZATES PRODUCED BY MEANS OF TETRAMETHYLTHIURAM MONOSULFIDE AND SULFUR. (ZINC DITHIOCARBAMATE IN MOLE-PER CENT OF THE ADDED THIURAM MONOSULFIDE.)

Composition of the mixture: 4.16 g. tetramethylthiuram monosulfide; 0.64 g. sulfur, 8.15 g. ZnO, and 187 g. pale crepe (10^{-4} gram-atom S and 10^{-4} mole thiuram monosulfide per gram of mixture).

Cure (min.)	Dithiocarbamate in mole-% at temperature (° C)						
	90°	100°	110°	120°	130°	140°	150°
5							14.5
10					12.2	4.1	26.8
15						14.1	43.0
20		0.8		5.6		22.5	48.0
25							52.6
30					32.0	36.5	56.8
35			9.0				
40		2.2		15.9		45.5	
50					43.6		
60				26.1	45.8	52.3	
70		4.2	18.7		51.5		63.0
80				33.8		55.5	
100		6.0	24.3	40.5	56.0	57.5	63.5
120	4.9					58.2	
130		8.5	28.3		59.0		
160		10.9	33.5	49.3		60.0	
200		15.3	38.6				
210					62.5		
240	10.6	19.0	42.8	55.0		61.5	
280		21.8					
300					63.3		
320				60.8		62.5	
340			50.3				
360	14.3						
400		28.5		63.7			
480	17.8						
540		38.3					
600	22.7						
720	25.7	42.4	61.6	64.9	65.0		
900		50.1	64.3				
1200	37.7						
1260		55.6					
1620		61.5					
1800		61.0					
2000			67.1				
2100	51.6						
2160		64.9					
2880		67.2					
3000	58.0						
4200	65.3						
6000	69.5 (?)						
9000	71.5 (?)						

Figure 1 shows the conversion curves. The abscissa gives the vulcanization time in minutes, the ordinate the zinc dithiocarbamate in mole-per cent of the initial thiuram monosulfide. Two molds were used, *a* and *b*, of different size but of similar type (weight of the forms *a* and *b*, 5.2 and 0.9 kg., respectively). Because of the difference in the "warm-up time" caused by this, i.e., the time from the instant the molds were put into the thermostat until the test temperature was attained in the interior, the curves designated by "a" or "b" are only in the proper order with respect to each other. For this reason, moreover, the results obtained at the vulcanization temperature of 140° C (see Table 1) are not given in Figure 1. They were obtained by using form *a*, and give a conversion curve which would approach too closely to the curve found for the results obtained with form *b* at 130° C.

In spite of the relations caused by the discrepancy in the warm-up times resulting from the use of forms of different weight, Figure 1 shows the essential

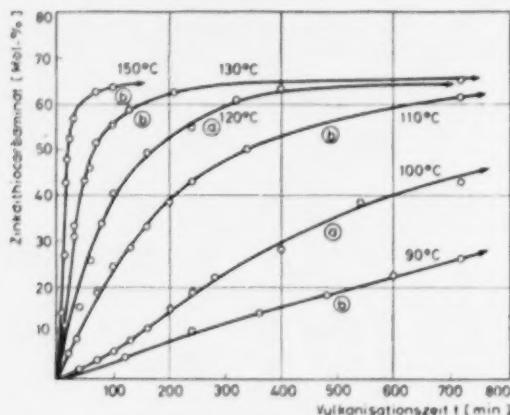


FIG. 1.—Increase of concentration of zinc dithiocarbamate with time of vulcanization at different temperatures (vulcanization with thiuram monosulfide and sulfur).

features. As in the vulcanization by thiuram disulfides, we have the formation of zinc dithiocarbamate, which increases with the reaction time, and the higher the vulcanization temperature, the more rapidly it proceeds. It is evident that all the conversion curves again approach a common limiting value, a fact that is especially clear when one looks at the curves for 110°, 120°, 130°, and 150° C. On closer inspection of the conversion curves for 100° and 90° C, however, slight differences can be seen between the thiuram disulfide vulcanization and that produced by thiuram monosulfide and sulfur (see the conversion curves of our earlier papers). The curve for 100° C, for example, shows in the region of short vulcanization times a slight sag toward the abscissa; that is, the formation of dithiocarbamate here evidently takes place a little more slowly than one would expect if the same conditions prevailed in every respect as in the vulcanization with thiuram disulfide. To be sure, this deviation shows up less distinctly at 90° C. It is evidently caused by a reaction of the monosulfide with sulfur, which precedes the formation of the dithiocarbamate and which is certainly a bimolecular reaction. This may proceed relatively slowly at lower

temperatures and, hence, have some influence on the characteristics of the conversion curves.

Figure 2, in which the abscissa is the reciprocal of the vulcanization time, the ordinate is the logarithm of the mole-per cent of zinc dithiocarbamate, makes it clear that, as in the vulcanization of natural rubber with thiuram monosulfide and sulfur, about 66 mole-per cent of zinc dithiocarbamate is formed, independent of the temperature. But this must presumably be regarded as proof that vulcanization by thiuram monosulfide and sulfur is nothing else than vulcanization by thiuram disulfide. Otherwise, one could not explain why the same relationships obtain as in the vulcanization with thiuram disulfides. There we may also conclude that the thiuram monosulfide together with sulfur is quantitatively converted to thiuram disulfide, that is, it enters into

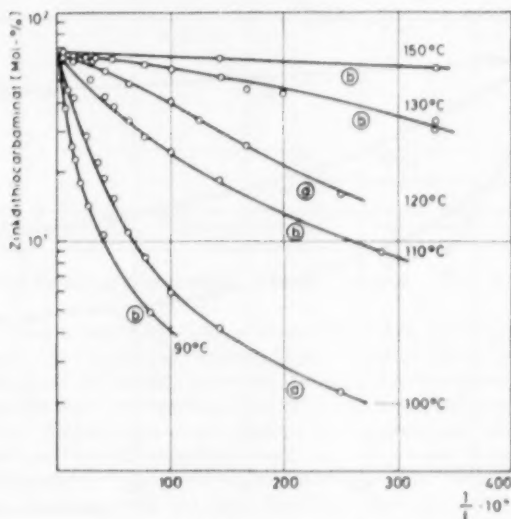


FIG. 2.—Demonstration that the limiting value of the yield of zinc dithiocarbamate is practically independent of the temperature.

no other reactions and also undergoes no thermal splitting. For if this were the case, the limiting value of the dithiocarbamate yield would have to be smaller. The complete conversion of the thiuram monosulfide with sulfur, which is a conclusion made necessary by the experimental results, must be emphasized, since, in the vulcanizates which have not reacted to completion, zinc dithiocarbamate occurs along with thiuram monosulfide and sulfur, and it would therefore be entirely possible that the thiuram vulcanization would be masked by a vulcanization of the rubber by sulfur, accelerated by zinc dithiocarbamate, which would unquestionably bring about other relationships. But, as one sees, this is not the case, at any rate provided the thiuram monosulfide and sulfur are present in the proportions corresponding to the formation of thiuram disulfide. Whether, on the other hand, the relationships change if the proportions of the two components become incommensurable would have to be learned from further studies.

Figures 3 and 4, in which the abscissa is the vulcanization time in minutes, the ordinate the logarithm of the concentration of the zinc dithiocarbamate ($66.6 - x$) in mole-per cent, show that the formation of dithiocarbamate in the present case can be similarly described, over an extended range of different concentrations, as a first-order reaction. Departures from this, which show up especially clearly at 120° and 140° C (Figure 3) and at 130° and 150° C (Figure 4), can be interpreted, as we established in another paper⁶, as a consequence of the influence on the vulcanization of the diffusion of the reaction partners in the highly viscous medium.

In Figure 3 the results of all the series of experiments carried out with the use of the larger mold are presented graphically. The curves do not intersect the ordinate for $t = 0$ at 66 mole-per cent, but instead reach the limiting value

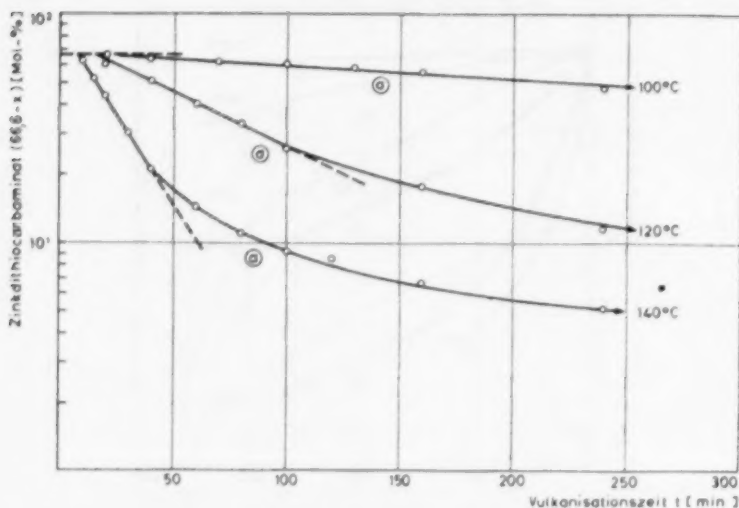


Fig. 3.—Formation of zinc dithiocarbamate in the vulcanization of rubber with thiuram monosulfide and sulfur as a first-order reaction. Experiments with form a. With a warm-up period.

of the dithiocarbamate formation at finite values of t . This is, without doubt, to be attributed to the fact that a measurable time elapses before the material in the interior of the mold has reached the vulcanization temperature. This time depends on the temperature at which the experiment is carried out, and is greater the lower the temperature. In the plots of the experimental results according to a conversion of the first order, the only effect of the existence of a warm-up time is to displace the curves along the axis.

Figure 4, on the other hand, shows that in experiments with the much smaller form, *b*, the warm-up times are no longer apparent, for the linear portions of the curves can be extended to intersect the ordinate at 66 mole-per cent. It is seen that the errors, which can always arise by reason of the heating up of the molds in vulcanizations carried out in this way, and which make the precise time of the start of the reaction uncertain, can be reduced to a minimum by using sufficiently small molds. We could also have made the conditions still

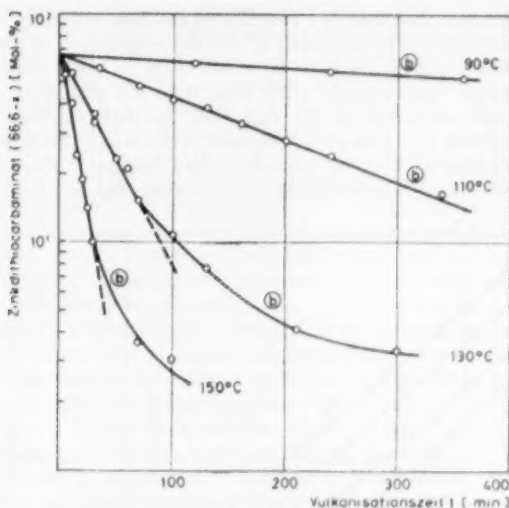


Fig. 4.—Formation of zinc dithiocarbamate in the vulcanization of rubber with thiuram monosulfide and sulfur as a first-order reaction. Experiments with form b. With no warm-up period.

more favorable by using thermostats of larger volume. This was, however, not practicable.

The fact that a warm-up time is observed in the investigations described here under suitable conditions, whereas it is not noticeable in the vulcanization with thiuram disulfides⁷ must, moreover, be related to the formation of thiuram disulfide from thiuram monosulfide and sulfur as a preliminary stage to actual vulcanization. As has been shown also in the present case, the thiuram disulfide which effects the vulcanization must only be formed progressively in the course of the reaction. Its initial concentration is zero. If, on the other hand, vulcanization is made with thiuram disulfide, then the vulcanizing agent is present in advance in high concentration, and the error resulting from the warm up time must necessarily be smaller. Moreover it will possibly be partially compensated by a slight formation of dithiocarbamate in the mixing itself.

It is remarkable that the formation of zinc dithiocarbamate in the vulcanization of natural rubber by thiuram disulfides, as well as in the interaction of

TABLE 2

VELOCITY CONSTANTS OF THE FORMATION OF DITHIOCARBAMATE IN THE VULCANIZATION OF NATURAL RUBBER WITH TETRAMETHYLTHIURAM MONOSULFIDE AND SULFUR (1 MOLE THIURAM MONOSULFIDE PER GRAM-ATOM OF SULFUR)

Temperature (°C)	Reaction velocity constants k_{inc}
90°	6.92×10^{-4}
100°	1.51×10^{-3}
110°	4.25×10^{-3}
120°	1.10×10^{-2}
130°	2.11×10^{-2}
140°	3.64×10^{-2}
150°	6.70×10^{-2}

geraniol with thiuram disulfide, is a reaction of the first order, for one must take into consideration that it is the result of the decomposition of an intermediate compound, which must be assumed to exist, since in both cases the thiuram disulfide disappears more rapidly with time than the dithiocarbamate is produced. Still more surprising is the fact that the dithiocarbamate formation can still be described as a first-order reaction, even when the interaction of the thiuram monosulfide with sulfur precedes vulcanization. Even the deviation from the normal characteristics of the other curves that is peculiar to the con-

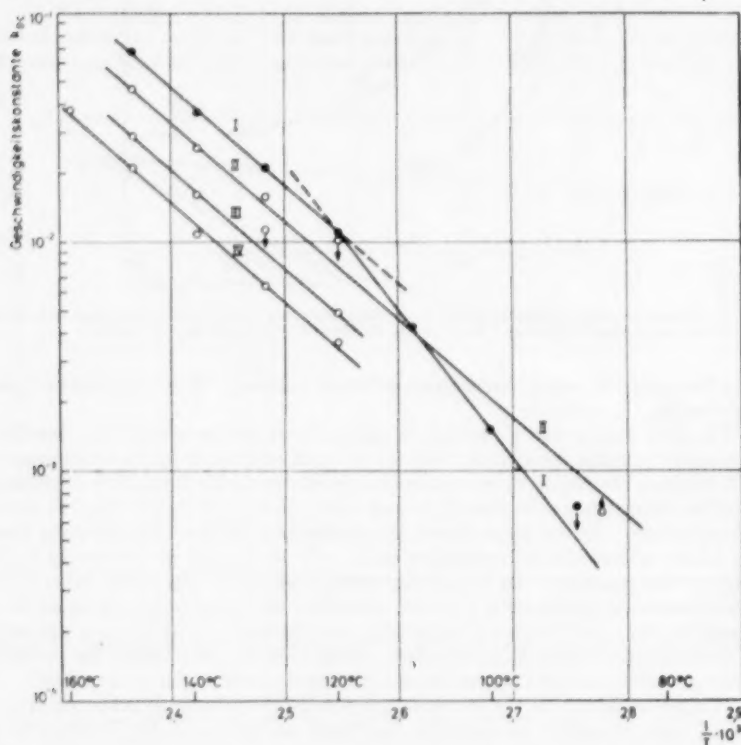


Fig. 5.—Temperature dependence of the velocity constants of the formation of dithiocarbamate in vulcanization with thiuram monosulfide and sulfur (curve I) and in vulcanization with tetramethyl-, tetraethyl-, and tetrapropylthiuram disulfides (curves II, III, and IV).

version curve for 100° C (Figure 1) has no notable influence on the plotting of the experimental results according to a reaction of the first order.

It is only when one examines the velocity constants of Table 2 calculated from the values of Table 1 and the curves of Figures 3 and 4 with respect to their temperature dependence that the influence of the earlier reaction becomes evident. This is shown by Figure 5, in which the ordinate gives the logarithm of the velocity constants k_{DC} , the abscissa the reciprocal of the absolute temperature.

It is noted that the velocity constants of the dithiocarbamate formation in

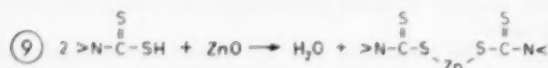
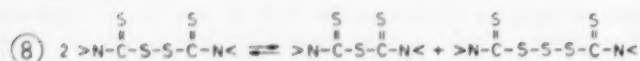
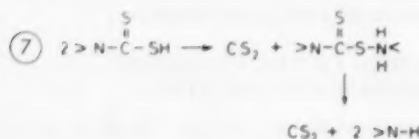
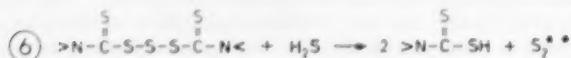
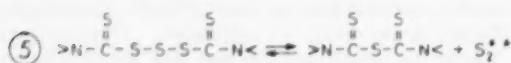
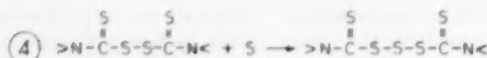
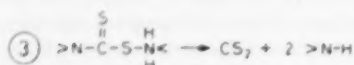
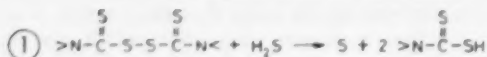
the vulcanization with thiuram monosulfide and sulfur (curve I) are greater than those in the vulcanization with tetramethylthiuram disulfide (curve II). This may be explained in one way on the basis that the number of configurations favorable to the reaction is greater when monosulfide and sulfur are present than when the disulfide is introduced initially (frequency factor). Such an interpretation is in harmony with the fact that, in this temperature region, the preliminary reaction is still without influence on the energy relationships, for between 120° and 150° C the velocity constants lie on a straight line (I) which runs parallel to the curves II, III, and IV, namely, to the temperature functions of the velocity constants of the dithiocarbamate formation in the vulcanization with tetramethyl-, tetraethyl-, and tetrapropylthiuram disulfide⁸. In this region, therefore, the same relationships with respect to energy, hold as in thiuram disulfide vulcanization. This only serves to emphasize the conclusions already drawn from the results of the present investigation. But at temperatures below 120° C, significant departures occur. The temperature dependence of the velocity constants here no longer follows the straight line (I); instead there is a different larger energy of activation. The energy relationships are changed. Under the conditions this can only be an influence of the preliminary reaction of the thiuram monosulfide with sulfur⁹. We do not care at present, however, to attempt any detailed explanation of this phenomenon. Moreover it does not affect the result which has been of primary interest to us, according to which, in vulcanization by thiuram monosulfide, the real vulcanization is fundamentally one produced by thiuram disulfide.

THE PROBLEM OF THE CHEMISTRY OF THIURAM VULCANIZATION

The vulcanization of natural rubber by thiuram disulfides as well as by mixtures of thiuram monosulfide and sulfur has, ever since its discovery, been the object of numerous investigations, both in this and in other countries⁷. The interpretation which has been tenaciously held is the one according to which what happens is a result of transformations of the unquestionably very sensitive and very reactive thiuram compounds but where free sulfur is the final vulcanizing agent.

Unfortunately, in the researches into the vulcanization mechanisms, the conventional physical and technical properties of the vulcanizates have generally been used as criteria, and too little effort has been made to gain an insight into the chemical transformations which come into play in vulcanization. Quite apart from the fact that a modulus measured in the usual way, for example, does not reflect exclusively the changes produced by vulcanization in the supermolecular structure of the rubber, it is certainly very questionable whether the course of the chemical reactions occurring during vulcanization are reflected in the variation of the modulus with length of vulcanization time. Nevertheless Craig and his coworkers¹⁰ have recently studied the chemical properties of thiuram compounds more intensively, and, on the basis of the results obtained, they have taken a stand with regard to the question of the mechanism of thiuram vulcanization. For isolating the compounds formed in the course of the vulcanization, they used the short-path distillation. We are not, to be sure, fully convinced that this is applicable in this case. Their publications also lack clarity, so that it is hard to grasp the authors' concept. Nevertheless we believe we can infer from their accounts that they too assume that thiuram vulcanization is essentially brought about by sulfur.

REACTION MECHANISMS OF THIURAM VULCANIZATION ACCORDING TO CRAIG AND COWORKERS



In the proposed mechanism developed by Craig and his coworkers, an important role seems to be played by the assumption, which is made by other experimenters as well, that a slight amount of hydrogen sulfide is formed (H_2S initiation). The authors claim that the hydrogen sulfide, along with other products, can be formed in the course of a direct interaction of the thiuram disulfide with α -methylene groups of the polyisoprene chain molecules. But for this, however, it is necessary, in our opinion, to assume that thiuram disulfide breaks down into thiuram monosulfide and sulfur and that the sulfur dehydrogenates the macromolecules. However that may be, in the presence of zinc oxide the concentration of the hydrogen sulfide is supposed to be slight, but nevertheless sufficient to produce an appreciable interaction with thiuram disulfide (1) (see the collection of formulas). Then the sulfur which appears along with dithiocarbamic acid or dialkylammonium dithiocarbamate (2) as well as dialkyl amine (3) and carbon disulfide is supposed to interact with thiuram disulfide to form thiuram trisulfide (4), whose existence, to be sure, could not be demonstrated. Then the authors postulate that this will come

into equilibrium with thiuram monosulfide and free radicals of the S_2 (5). In addition to all this, they also consider possible a reaction of the thiuram trisulfide with hydrogen sulfide, a reaction analogous to (1), with the subsequent reaction corresponding to (7) analogous to (6).

It is seen that Craig and coworkers believe the sulfur, which in their view is what principally brings about the cross-linking even in thiuram vulcanization is produced along with other products by conversions (5) and (6). However, they also discuss an equilibrium between thiuram disulfide, thiuram monosulfide, and thiuram trisulfide (8), which furnishes the sulfur necessary for their theory of thiuram vulcanization, even without initiation of the total process by hydrogen sulfide, namely, by the splitting of the thiuram trisulfide in (8) according to reaction (5) into monosulfide and sulfur. This process is not capable, however, of accounting for the formation of the principal, if not indeed the only reaction product in thiuram vulcanization, namely, dithiocarbamic acid, unless it is also assumed that the sulfur being formed also has a simultaneous dehydrogenating action on the rubber.

The formation of secondary amine, in accordance with reactions (2), (3), and (7), could, if we have correctly understood the exposition of Craig, occur especially in the absence of zinc oxide, but then be subject to further interactions with thiuram disulfide, which would be without vulcanizing effect ("vulcanization-indifferent"); for useful vulcanizates are obtained in the absence of zinc oxide only with high concentrations of thiuram disulfide. On the other hand, in the presence of zinc oxide, there can hardly be a formation of secondary amine. One must certainly expect that the dithiocarbamic acid formed in the course of reactions (1) and (6) will then be combined as zinc dithiocarbamate (9). We believe, therefore, that, in thiuram vulcanization, one cannot speak of zinc oxide as an activator, but it has, in our opinion, only the function of combining with the dithiocarbamic acid, which would otherwise cause undesired side reactions. Thus it is better described as a basic raw material.

With this interpretation of thiuram vulcanization as it has been developed by Craig and coworkers and sketched here in rough outlines, it would hardly be possible to account for the quantitative results of our investigation in this field. One is faced with the problem of having to explain, by a dubious reaction, not only the conversion of thiuram disulfide, but now, in addition, that of the monosulfide as well to zinc dithiocarbamate. The conversion of the thiuram disulfide is considerable, amounting to about 66 mole-per cent, and is independent of the temperature. Zinc dithiocarbamate is the principal extractable reaction product of thiuram vulcanization. This dubious reaction, which has certainly not been established and is, therefore, in our opinion a hypothetical one, is the formation of hydrogen sulfide and its reaction with thiuram disulfide according to reaction (1). Even if it is assumed that the sulfur appearing in the course of the conversions postulated by Craig and coworkers can act not only to form bridges but also to dehydrogenate, the conversion of the hydrogen sulfide that appears during the dehydrogenation will only be negligible, for one must certainly reckon with the fact that most of it would be combined with the zinc oxide to form the sulfide. Moreover, Craig and coworkers themselves explain that the hydrogen sulfide concentration at any instant needs to be only slight, and in the presence of zinc oxide will indeed be so. For this reason, however, we believe that the formation of such large amounts of dithiocarbamate in a vulcanization carried out with zinc oxide present can hardly be regarded as produced by a reaction of hydrogen sulfide with thiuram disulfide. Besides this, no experimental proof can be found that makes the formation of

hydrogen sulfide seem probable, and, in our opinion, there is no compelling reason for such an assumption.

One can certainly better explain the formation of the thiocarbamic acid by a reaction of the free radicals of the thiuram disulfide ($=N-C(S)-S^*$) with the α -methylene groups of the polyisoprene. The thiuram free radicals here go over into dithiocarbamic acid, which combines as zinc dithiocarbamate. Besides this, polyisoprene free radicals appear and play a role in the cross-linking. Even though we still cannot make any definitive statement as to how the reaction of the thiuram free radicals with the rubber takes place, a reaction which moreover cannot be exclusively one of dehydrogenation, and how a two-thirds conversion of the thiuram disulfide to dithiocarbamate results, we should like, nevertheless, to point out that our concept is worthy of discussion because there exists a certain analogy between the reaction of thiuram disulfide and that of benzoyl peroxide with natural rubber.

According to more recent investigations in our institute¹¹, benzoyl peroxide, like thiuram disulfide, also decreases during vulcanization according to a first-order reaction, and whereas dithiocarbamic acid is formed in thiuram vulcanization, in the peroxide vulcanization benzoic acid is produced, and in fact, as is true of the dithiocarbamic acid in thiuram vulcanization, also according to a first-order reaction. The formation of the dithiocarbamic acid takes place more slowly than the decrease of concentration of the thiuram disulfide. In a corresponding manner, in the peroxide vulcanization, the appearance of benzoic acid is the slower process. A portion of the benzoyloxy radicals remain bound in the rubber¹², and the possibility that, in thiuram vulcanization, thiuram-free radicals remain bound in the vulcanizate is not to be dismissed in view of the combined sulfur content of the extracted thiuram vulcanizates. Thus the analogy of the two vulcanization reactions is unmistakable.

Now it seems that it can hardly be doubted that the vulcanization of rubber by peroxides is a polymerization induced by the particular peroxide of the 1.5 diene units of the polyisoprene, and therefore, because of the formal analogy between thiuram and peroxide vulcanization with respect to kinetic relationships, we are led to suppose that thiuram vulcanization is to be conceived, qualitatively at any rate, as like peroxide vulcanization¹³.

Coming back to the further reactions formulated by Craig and coworkers, we do not consider their course during vulcanization as probable. If, for example, we assume that reactions (4) and (5) were essential processes in thiuram vulcanization, then we should expect that the extracts of the vulcanizates would contain amounts of thiuram monosulfide which increase with increase of the time of the reaction, for the formulations finally imply that thiuram disulfide is to act as sulfur transmitter. On the contrary, neither we nor Jarrión⁴ were able to detect thiuram monosulfide in the extracts. Besides this, the results of the present investigation show that thiuram monosulfide in the vulcanization with sulfur goes over into thiuram disulfide, and only this can be the vulcanizing agent. For, to stress this once more, vulcanization by thiuram monosulfide and sulfur gives the same relationships as those in the vulcanization with thiuram disulfide. If, however, one adheres to the idea of the simultaneous occurrence of all the reactions (1) through (8) discussed by Craig and coworkers, then, as is easily seen, it cannot be understood why the final dithiocarbamate yield is so large and why it is practically independent of the temperature.

In conclusion, we should thus like to express the fact that we cannot subscribe to the mechanism of thiuram vulcanization developed by Craig and co-

workers, a mechanism, which to be sure, does not differ essentially from that which has long prevailed. Although we certainly value highly the careful study of the reactions of thiuram compounds made by Craig and coworkers, we cannot accept the concept according to which thiuram vulcanization is supposed to involve principally vulcanization by sulfur. That we for the present have no occasion to accept it must be clear to every careful reader of our works. We should like, on the contrary, to ask that it be considered whether it is not better to discuss a polymerization of the polyisoprene induced by free radicals of the thiuram disulfide, in which both double bonds and also α -methylene groups are attacked by the free radicals.

SUMMARY

The vulcanization of natural rubber (pale crepe) by tetramethylthiuram monosulfide and sulfur (1 mole monosulfide per gram-atom of sulfur) has been studied in the temperature range from 90° to 150° C. The following results were obtained:

1. During vulcanization, the concentration of the thiuram monosulfide and also of the sulfur decreases.

2. In accordance with a first-order reaction, about 66 mole-per cent of zinc dithiocarbamate is formed (calculated on the amount of thiuram monosulfide added). Thus the same relationships were found as in vulcanization with thiuram disulfides.

3. The vulcanization of rubber with thiuram monosulfide and sulfur is, therefore, nothing else than vulcanization by thiuram disulfide, whose quantitative formation precedes the actual vulcanization reaction.

4. In no stage of vulcanization could thiuram disulfide be detected with certainty in the extracts of the vulcanizates. It must be assumed, therefore, that it reacts with the rubber instantly after it is formed.

5. The velocity constants derived for the dithiocarbamate formation at the various temperatures both from the experimental results and from the graphical presentations have been given, and their temperature dependence has been discussed. At lower temperatures, the influence of the prior interaction of the monosulfide with sulfur makes its influence on the energy relationships felt.

6. It is once more emphasized that in thiuram vulcanization it cannot be a question of a vulcanization with sulfur. In this connection we take a decided stand also with regard to the results of the more recent investigations of Craig and his coworkers.

ACKNOWLEDGMENTS

This work has been carried out with the support of the Rubber Central Research Laboratory of the Bayer AG. Dye Works (Farbenfabriken), Leverkusen, and of the Continental Gummi-Werke AG, Hannover. We should like to express here our heartfelt thanks to both firms for providing us with natural rubber and chemicals.

One of us (Scheele) is indebted to Prof. Dr. F. Palat for stimulating discussions.

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- ⁴ See the corresponding figures in Scheele, Lorenz, and Dummer, *Kautschuk u. Gummi* 8, WT 2 (1955); this issue *RUBBER CHEM. & TECHNOL.*
- ⁵ Scheele, Lorenz, and Dummer, *Kautschuk u. Gummi*, 8, WT 27 (1955); this issue *RUBBER CHEM. & TECHNOL.*
- ⁶ Concerning deviations of the temperature function of the velocity constants of the straight lines in parallel reactions, see Hinshelwood, "The Kinetics of Chemical Change", Oxford, 1942, p. 45.
- ⁷ Craig et al., *J. Polymer Sci.* 5, 709 (1950); 6, 1, 7, 13, and 177 (1951); 8, 321 (1952).
- ⁸ These studies by Lorenz and Scheele, which have only recently been provisionally completed, will soon be reported in detail in *Kautschuk u. Gummi*.
- ⁹ Attention has been called by van Rossem, Dekker, and Prawirdiporo (*Kautschuk* 7, 219 (1951)) to the formation of benzoic acid and to the fact that benzoyloxy free radicals remain bound in the vulcanizate. Farmer and Michael (*J. Chem. Soc.*, 1947, p. 513) investigated the reaction of benzoyl peroxide with cyclohexene as a model compound. Their investigations showed that a considerable amount of the peroxide remains bound in the rubber in the form of benzoate groups. They have also proposed a reaction mechanism for the vulcanization by benzoyl peroxide. According to this, the formation of benzoic acid is to be ascribed to interaction of benzoyloxy free radicals with α -methylene groups. Of interest also in this connection are the studies of Bartlett et al. (*J. Am. Chem. Soc.* 67, 812, 816 (1945)). The authors studied the kinetics of the polymerization of allyl compounds induced by benzoyl peroxide, and concerned themselves also with explaining the mechanism of this polymerization. They arrived at the result that the peroxide not only initiates a polymerization in the reaction of its free radicals with the double bonds, but also reacts with the α -methylene groups (formation of benzoic acid). The relationships are thus not unlike those in the peroxide vulcanization of rubber.
- ¹⁰ Farmer and Michael (*J. Chem. Soc.*, 1947, p. 513) state: "Perhaps, however, the most interesting example of an effective vulcanizing agent is tetramethylthiuram disulfide, which is a close sulfur analog of benzoyl peroxide. The capacity of this substance to yield free radicals spontaneously or on heating has, so far as we are aware, not been demonstrated, but it is remarkable that this disulfide is not only by itself an excellent vulcanizing agent for rubber, but is a first-rate accelerator of sulfur vulcanization. The method of action of accelerators has never been determined, but it seems not unlikely that the effectiveness of at least some of them is due to their capacity to yield free radicals spontaneously or on heating. . . ." We too are of this opinion.

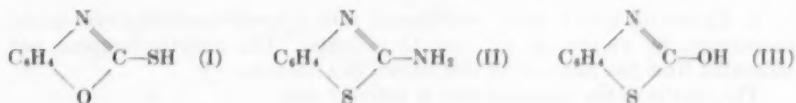
MECHANISM OF THE EXCHANGE REACTION OF ELEMENTAL SULFUR WITH MERCAPTOBENZOTHAIAZOLE *

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As was shown in our preceding study¹, a rapid exchange of sulfur atoms takes place between elemental sulfur and 2-mercaptobenzothiazole at temperatures corresponding to the conditions of vulcanization of rubber. This indicates the existence of a reaction between the atoms, and also the formation during this reaction of some kind of intermediate compounds. On the basis of the experimental data, it was established that only one of the sulfur atoms of mercaptobenzothiazole enters into the exchange reaction.

It was natural to assume, in view of the technical properties of derivatives of mercaptobenzothiazole and its own chemical properties, that the sulfur of the sulphydryl group takes part in the reaction. In fact, as is shown in another study², 2-mercaptobenzoxazole (I) has a stronger accelerating effect during vulcanization than 2-aminobenzothiazole (II) or 2-oxybenzothiazole (III).



Furthermore, it is known that the sulfur in the sulphydryl group of mercaptobenzothiazole and its derivatives is considerably more mobile than the sulfur in the ring, and is easily converted into other substituents.

However, our assumption required experimental confirmation. For this purpose, we oxidized mercaptobenzothiazole, after exchange with radioactive elemental sulfur, with potassium permanganate in an alkaline solution by the method of Efros and Davidenkov³.

Seven-tenths gram of active mercaptobenzothiazole was dissolved in a solution of 0.3 gram of potassium hydroxide in 5 cc. of water. The homogeneous mixture obtained was stirred continuously, and 14 cc. of a 10 per cent water solution of potassium permanganate, kept at 50-60°, was added. After 3 hours the solution was made colorless by the addition of a very small amount of oxalic acid, then acidified with hydrochloric acid (Congo red reaction), and then boiled until the odor of sulfur dioxide disappeared. The crystals of 2-oxybenzothiazole (III) precipitated during cooling were recrystallized from water, and then had a melting temperature of 135°.

The activity of 1 mg. of the original 2-mercaptobenzothiazole was 400 counts per minute; 2-oxybenzothiazole gave 23 per minute per mg. The reading of the counter itself was equal to 23 counts per minute. Consequently,

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Doklady Akademii Nauk SSSR*, Vol. 90, No. 2, pages 201-204 (1953).

there is no active sulfur present in 2-oxybenzothiazole. These data clearly show that only the sulfur atoms from the sulfhydryl group of 2-mercaptobenzothiazole enter into the exchange reaction with sulfur.

In order to investigate this reaction more thoroughly, we studied the exchange between elemental sulfur and benzothiazole derivatives which do not contain mercapto groups. The following experiments were carried out.

1. Active sulfur and 2-aminobenzothiazole (II), in equal proportions by weight, were fused at 140° for 15, 30, and 75 minutes, and also at 150° for 45 minutes. The 2-aminobenzothiazole was separated from the mixture by dissolving it in water and then evaporating the solution in a water bath. The product obtained was dried to constant weight, and its activity was measured with a Geiger-Müller counter.

The following results were obtained:

	Number of counts per minute per mg.
Activity of original sulfur	200
Activity of 2-aminobenzothiazole, separated from fusion after heating at 140°:	
15 minutes	15
30 minutes	16
75 minutes	16
Dial reading of counter 15	15-16
Activity of 2-aminobenzothiazole separated from fusion after heating for 45 minutes at 150°	37
Dial reading of counter	35

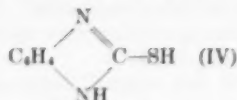
2. Elemental active sulfur was heated with 2-methylbenzothiazole (equal proportions by weight) at 137° for 15 minutes. The 2-methylbenzene was separated from the mixture by distillation in a vacuum.

The results of the measurement of activity were:

	Number of counts per minute per mg.
Activity of original sulfur	172
Activity of 2-methylbenzothiazole	28
Dial reading of counter	28

From this series of experiments it is evident that the sulfur in the thiazole ring of benzothiazole derivatives is not capable of an exchange reaction with the elemental sulfur in the time and temperature range studied. All these experiments confirm our basic premise that only the sulfur of the sulfhydryl group of mercaptobenzothiazole takes part in exchange reactions with sulfur.

On the other hand, 2-mercaptobenzoimidazole (IV), used as an age resistor in colored vulcanizates, although containing a sulfhydryl group, does not take part in exchange reactions with sulfur at vulcanization temperature.



2-Mercaptobenzoimidazole (0.1 gram) was fused with active sulfur (0.2 gram) at 172° for 30 minutes. The mercaptobenzoimidazole was separated from the mixture, after the latter had been finely ground, by extraction with a

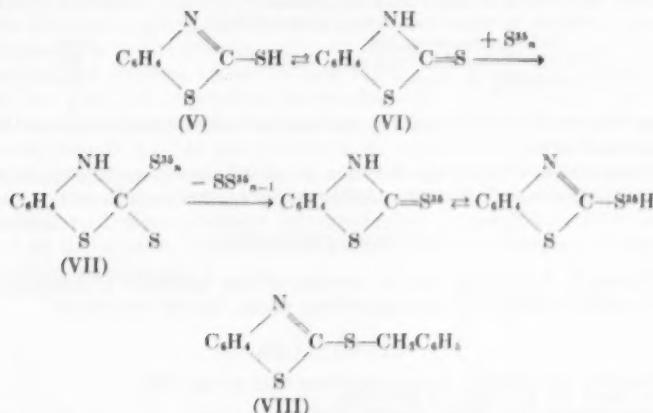
5 per cent water solution of sodium hydroxide, followed by neutralization of the extract with hydrochloric acid. The product separated was filtered, rinsed, and dried.

The results of measurement of the activity of the compounds follow:

	Number of counts per minute per mg.
Activity of original sulfur	280
Activity of 2-mercaptobenzimidazole	21
Dial reading of counter	21

The absence of an exchange reaction in this case can be explained by the high melting point of 2-mercaptobenzimidazole (270–272°). According to our preliminary experiments, a noticeable exchange with elemental sulfur is already observed at a temperature about 250°.

On the basis of the results of our experiments as presented above, it is possible to assume the following mechanism of exchange reactions between elemental sulfur and mercaptobenzothiazole. We ascribe the exchange to the tautomerization of 2-mercaptobenzothiazole (V) into a thionic structure, forming an intermediate di- or polythionic complex with the elemental sulfur (VII).



Preliminary conversion into a thionic structure is in fact necessary, since 2-benzylmercaptobenzothiazole (VIII), being incapable of such tautomerization, does not exchange its sulfur atoms with the elemental sulfur. When active sulfur (0.1 gram) is fused with 2-benzylmercaptobenzothiazole (0.7 gram) in a sealed tube at 150°, the ether separated from the mixture contains no active sulfur, as is seen from the data below.

	Number of counts per minute per mg.
Activity of ether separated from mixture	
without heating	24
heated to 40°	22
heated to 150°, ½ hour	17
heated to 150°, 1 hour	35
heated to 150°, 3 hours	42

The original sulfur gave 2800 counts in 10 minutes per mg. The ether separated from the mixture after heating for 3 hours at 150° and repeated re-

crystallization from 60 per cent alcohol gave 26 counts in 10 minutes per mg. All the data allow for the dial reading of the counter.

The ether was separated from the mixture by extracting with an 80 per cent hot alcohol-water solution. When the ether is separated as described, a small amount of active sulfur remains in it, as is seen from the data on the activity of ether extracted from the mixture without heating. However, when the mixtures are heated, the activity of the ether does not increase; this indicates the absence of exchange reactions. It should be noted that 2-benzylmercapto-benzothiazole has no accelerating effect on the vulcanization of rubber, as Zeide and Galanov have shown⁴.

The possibility of sulfur exchange in the C=S bonds was studied by the authors for the case of exchange reactions of sulfur with thiourea. For this purpose, active sulfur (0.11 gram) was fused with thiourea (0.25 gram) at 183° for 30 and 60 minutes. The thiourea was separated from the sulfur by extraction of the fusion mixtures with water.

The following results were obtained:

	Number of counts per minute per mg.
Activity of sulfur from fusion after heating for 30 minutes at 183°	145
Activity of thiourea from same fusion	64
Activity of sulfur from fusion after heating for 60 minutes at 183°	149
Activity of thiourea from same fusion	60
Dial reading of counter	25

These data indicate an intensive exchange of sulfur atoms between thiourea and elemental sulfur.

The mechanism of exchange reaction proposed above must be regarded as a working hypothesis. It must be confirmed by further experiments.

ACKNOWLEDGMENT

We thank A. I. Brodski, active member of the Academy of Sciences of the USSR, in whose laboratory this study was made, for his assistance.

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THE MOBILITY OF SULFUR BONDS IN SOFT RUBBER AND EBONITE *

G. A. BLOKH AND L. F. CHUPRINA

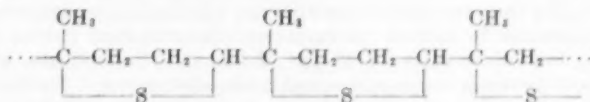
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Much attention has been devoted to the problem of the sulfur and oxygen bonds in vulcanized rubber in numerous studies of both Soviet and foreign scholars. In the Soviet Union, the works of a large group of investigators, including B. A. Dogadkin, A. D. Zatonchovskii, P. A. Rebinder, A. P. Pisarenko, A. S. Kuzminskii, and others, have dealt with this problem.

The nature of the sulfur structures formed in soft vulcanized rubbers depends on a number of factors, including the nature of the accelerators. It was shown in one work¹ that sulfur vulcanization in the absence of sulfur-bearing accelerators leads to the formation of relatively weak polysulfide bonds. We assume that here a group of different polysulfide bonds is formed at the expense of the passage of octatomic ring sulfur structures into open linear sulfur radicals. For vulcanized rubbers which contain sulfur and diphenylguanidine in their recipe, the group of polysulfide bonds evidently constitutes an excellent criterion of their characteristic vulcanization structures. A number of rubber products, including cable and insulation rubbers, which do not contain sulfur as a vulcanizing agent are also known. In this case vulcanization takes place at the expense of the decomposition of tetramethylthiuram disulfide (thiuram vulcanization). Here stronger intermolecular monosulfide sulfur bonds are formed at the expense of the atomic sulfur, which is liberated during the decomposition of thiuram:



The sulfur structures are altogether different in the case of ebonite². The structure of natural-rubber ebonite has been studied by the method of pyrolysis. Study of the products of pyrolysis of ebonite has shown that, in ebonite, the sulfur is bound intramolecularly with the tertiary carbon atom, that is, the sulfur atom unites not two neighboring carbon atoms, but those separated from each other by two methylene groups, forming thiophene groups in the ebonite structure.



The structure of the sulfur bonds in synthetic-rubber ebonites has not been studied.

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY from the *Doklady Akademii Nauk SSSR*, Vol. 99, No. 5, pages 575-760 (1954).

The differences between the structures of the sulfur bonds of soft vulcanized rubbers and ebonites must also be reflected in the mobility of these bonds. In a previous work³ we showed, by means of radioisotopic sulfur, that vulcanizates of natural rubber and synthetic rubbers (SKB, SKS-30) prepared with only radiosulfur or sulfur and diphenylguanidine, were characterized by the presence of mobile polysulfide sulfur. Radiovulcanizates from which the free sulfur had been eliminated by prolonged extraction with acetone were then boiled in alcohol and xylene solutions of various non-radioactive accelerators (mercaptobenzothiazole, benzothiazolyl disulfide, tetramethylthiuram disulfide, sodium carbamate, sulfenamide, etc.). The above mentioned accelerators were then found to be radioactive. This indicates the existence of exchange reactions (the percentage of exchange varied within wide limits, and reached as high as 12). It was shown that vulcanizates in which the polysulfide bonds were destroyed by prolonged boiling in a 10 per cent solution of sodium sulfite did not take part in the exchange reactions.

The following study is devoted to the mobility of the bound sulfur in thiuram vulcanizates and ebonite.

STUDY OF THIURAM VULCANIZATES

Thiuram vulcanizates were prepared (6 grams of tetramethylthiuram disulfide per 100 grams of polybutadiene rubber). The vulcanizates were extracted with acetone for 50 hours in order to eliminate the sulfur-containing products of the decomposition of the thiuram compound. Failure to eliminate these products from the vulcanizate might lead to false conclusions about the mobility of monosulfide bound sulfur, since these products might take part in exchange reactions. In earlier works⁴ it was shown that the sulfur atoms present in the tetramethylthiuram disulfide structure are intensively exchanged with both the free sulfur and the sulfur in the mercapto group of mercaptobenzothiazole. Mercaptobenzothiazole, labeled in the sulfhydryl group, was synthesized by a method described earlier⁵. In the same work it was first proved experimentally that only the sulfhydryl sulfur of mercaptobenzothiazole possesses mobility. The sulfur of the thiazole ring is immobile. Our conclusions were repeated and confirmed in a later work⁶.

The activity of the original tagged mercaptobenzothiazole after a Carius combustion, determined in the form of benzidine sulfate, was 600 impulses per mg. The finely divided thiuram vulcanizate was extracted with acetone and then boiled in a solution of labeled mercaptobenzothiazole in xylene for 24, 48, and 72 hours. Then the mercaptobenzothiazole was separated from the xylene solution and its activity was measured. The activity of extracted mercaptobenzothiazole after boiling for 24 hours, determined in the form of benzidine sulfate, was 580 impulses per mg.; that is, it remained almost on a level with that of the original mercaptobenzothiazole. This demonstrates that the monosulfide-bound sulfur of a thiuram vulcanizate does not take part in exchange reactions. It was not possible to extract mercaptobenzothiazole from xylene solutions after boiling the vulcanizates for 48 and 72 hours. This indicates a possible chemical bond between mercaptobenzothiazole and rubber. Further experiments confirmed our hypothesis. A heat vulcanizate was prepared from polybutadiene rubber (100 grams) and radioactive mercaptobenzothiazole (3 grams). This was heated in an electric press for 120 minutes at 190° C. The sheets obtained were tested for radioactivity after every 8 hours of boiling in fresh lots of alcohol. Twelve alcohol extractions were made at 78° C, lasting

TABLE I

Duration of extraction (hours)	Radioactivity of film (imp. per mg.)	Duration of extraction (hours)	Radioactivity of film (imp. per mg.)
0	200	48	81
16	93	96	80
24	86	136	78

altogether 104 hours, and two butyl alcohol extractions at 117°, lasting 32 hours. It was not possible to extract the mercaptobenzothiazole from the sheets under these conditions, owing to their residual radioactivity.

It is seen from the data in Table I that most of the mercaptobenzothiazole was eliminated from the sheets by alcohol extraction for 16 hours. After that, the activity of the sheets, taking into account the natural degradation, changed very little. This indicates partial union of mercaptobenzothiazole with the rubber structure.

STUDY OF EBONITES

A specimen of unloaded ebonite, prepared by open-steam vulcanization of polybutadiene rubber and sulfur for 11 hours, was studied. The total sulfur content in the ebonite, determined by the Carius method, was 27.5 per cent. The sulfur content of the ebonite after extraction with acetone for 50 hours was 25.4 per cent. The sulfur content after extraction with acetone for 50 hours and then boiling for 54 hours in a 10 per cent solution of sodium sulfite was 22 per cent. The specimens, in the form of ebonite dust, after extraction with acetone, and also after extraction with acetone for 50 hours and boiling in a 10 per cent solution of sodium sulfate, were boiled for various periods in an *o*-xylene solution of tagged mercaptobenzothiazole (1.1314 grams of ebonite was boiled in 150 cc. of xylene, in which 300 mg. of radioactive mercaptobenzothiazole had been dissolved). Then the mercaptobenzothiazole was extracted and incinerated by the Carius method, and its activity was determined in the form of benzidine sulfate. The activity of the original mercaptobenzothiazole was 600 impulses per mg. The activity of the mercaptobenzothiazole after the ebonite specimens had been extracted for 50 hours with acetone and boiled for 2 hours was 440 impulses per mg. The activity of mercaptobenzothiazole after the ebonite specimens were boiled for 3 hours and after both extraction for 50 hours with acetone and boiling for 54 hours in a 10 per cent solution of sodium sulfate was 590 impulses per mg.

TABLE 2

Experimental conditions	Transfer (%)
I. Ebonite after 50 hours' extraction with acetone	
1st Boiling: 120 min. at 144° C	26
2nd Boiling: 240 min. at 144° C	9.9
3rd Boiling: 360 min. at 144° C	8.0
II. Ebonite after 50 hours' extraction with acetone and 26 hours' boiling in 10 per cent sodium sulfite solution	
Boiling 120 min. at 144° C	6.6
III. Ebonite after 50 hours' extraction with acetone and 54 hours' boiling in 10 per cent sodium sulfite solution	
Boiling 180 min. at 144° C	1.6

The results of the exchange in ebonites after extraction with acetone for 50 hours (see Table 2) can be attributed to the part played in the exchange by polysulfide sulfur and also, in part, by the residual free and adsorbed sulfur. Subsequent boiling of ebonite for 54 hours in a 10 per cent solution of sodium sulfite evidently made it possible to extract almost all the sulfur from the group of polysulfide bonds present, and also to extract all the possible free and adsorbed sulfur from ebonite. This makes exchange reactions practically impossible. Consequently, mobile polysulfide sulfur bonds are present in ebonite, along with intramolecular monosulfide sulfur bonds.

On the basis of the data obtained, one can conclude that monosulfide bound sulfur in both thiuram vulcanizates and in ebonites is strongly bound and immobile, and does not take part in exchange reactions.

ACKNOWLEDGMENT

We express our gratitude to corresponding member of the Academy of Sciences, A. I. Brodskii, for his advice and assistance in this work.

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OXIDATION OF ORGANIC SULFIDES.* III. A SURVEY OF THE AUTOXIDIZABILITY OF MONOSULFIDES

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The reactivity of organic sulfides towards molecular oxygen has not hitherto been investigated, despite its relevance to important industrial problems. Chief among these is the oxidative aging of ordinary (sulfur-cured) rubber vulcanizates, and here the omission has been partly deliberate in the sense that a rational approach has only become possible with recent advances in the understanding of the mode of sulfur combinations¹.

This paper reports a survey of autoxidizability of a number of saturated and unsaturated, cyclic and acyclic, monosulfides. We propose later to consider the influence of multi-sulfur linkages, the nature of the oxidation products, and the olefin-sulfide cooxidation system which a sulfur vulcanizate exemplifies.

EXPERIMENTAL


Alkyl- and Phenyl-substituted Sulfides.—Dibutyl, dibenzyl, and diphenyl sulfides were commercial specimens purified by conventional methods. Benzyl-*n*-propyl, methyl-1-phenyl-ethyl, and diphenylmethyl methyl sulfides were synthesized by standard methods. *n*-Butyl, methyl, and cyclohexylmethyl sulfides and 2-ethyl-2-methyl-5-isopropylthiacyclopentane were kindly provided by J. Ford, D. Barnard, and R. W. Glazebrook, respectively. The purified sulfides (see below) were characterized physically as shown in Table I; their purity was checked by analysis in all cases, but these data are given for the new compounds only.

TABLE I

	B. p./mm.	n_D^{20}	C (%)		H (%)		S (%)	
			Found	Reqd.	Found	Reqd.	Found	Reqd.
Bu ^a ·SMe	122.5°/760	1.4475	—	—	—	—	—	—
Bu ^a ·SBu ^a	71°/14	1.4525	—	—	—	—	—	—
Cyclo-C ₆ H ₁₁ ·SMe	62.5°/13	1.4945	—	—	—	—	—	—
CH ₃ ·CEtMe								
$\begin{array}{c} \text{CH}_3 \cdot \text{CHPr}^a \\ \diagup \quad \diagdown \\ \text{S} \quad \text{(I)} \end{array}$	87°/10	1.4760	—	—	—	—	—	—
CH ₃ ·CHPr ^a								
Ph·SPh	95°/0.02	1.6320	—	—	—	—	—	—
Ph·CH ₂ ·SPr ^a	110°/12	1.5429	72.2	72.2	8.5	8.5	19.5	19.6
Ph·CH ₂ ·S·CH ₂ Ph	(M. p. 49.5°)	—	—	—	—	—	—	—
Ph·CHMe·SMe	89°/12	1.5510	71.1	71.1	8.0	7.9	21.1	21.0
Ph ₂ CH·SMe	(M. p. 33°)	—	78.6	78.5	6.7	6.6	15.0	15.0

* Reprinted from the *Journal of the Chemical Society* (London), Part III from No. 5916, pages 1596-1603, May 1955 and Part IV from No. 5917, pages 1996-2005, June 1955.

TABLE 2

	B. p./mm.	n_D^{20}	C (%)		H (%)		S (%)	
			Found	Reqd.	Found	Reqd.	Found	Reqd.
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{SBU}^a$	73°/14	1.4677	—	—	—	—	—	—
$(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{S}$	33°/16	1.4905	—	—	—	—	—	—
$\text{CH}_2=\text{CH}-\text{CHMe}-\text{SBU}^a$	61°/15	1.4655	—	—	—	—	—	—
$\text{CHMe}=\text{CH}-\text{CH}_2-\text{SMe}$	126°/760	1.4780	58.9	58.8	9.9	9.9	31.1	31.3
$\text{CHMe}=\text{CH}-\text{CH}_2-\text{SBU}^a$	72°/14	1.4742	—	—	—	—	—	—
$\text{CHMe}=\text{CH}-\text{CH}_2-\text{SPh}$	50°/0.1	1.5695	—	—	—	—	—	—
$\text{CHMe}=\text{CH}-\text{CHMe}-\text{SMe}$	138°/749	1.4707	62.0	62.0	10.4	10.4	27.6	27.6
$\text{CHMe}=\text{CH}-\text{CHMe}-\text{SPr}^a$	60°/13	1.4688	66.4	66.6	11.2	11.1	22.3	22.3
$\text{CHMe}=\text{CH}-\text{CHMe}-\text{SPr}^i$	56°/17	1.4650	66.4	66.6	11.2	11.1	22.2	22.3
$\text{CHMe}=\text{CH}-\text{CHMe}-\text{SBU}^a$	81°/15	1.4688	68.2	68.3	11.5	11.4	20.1	20.3
$\text{CHMe}=\text{CH}-\text{CHMe}-\text{SBU}^i$	66.5°/13	1.4660	68.1	68.3	11.3	11.4	20.2	20.3
$\text{CHMe}=\text{CH}-\text{CHMe}-\text{SPh}$	118°/14	1.5542	73.9	74.1	7.9	7.9	18.1	18.0
 R	$\text{R}=\text{SMe}$	64.5°/14	1.5210	—	—	—	—	—
	$\text{R}=\text{SEt}$	76°/14	1.5140	—	—	—	—	—
	$\text{R}=\text{SPr}^i$	84°/14	1.5062	—	—	—	—	—
	$\text{R}=\text{SBU}^i$	97°/14	1.5015	—	—	—	—	—
	$\text{R}=\text{SPh}$	82°/0.005	1.5629	—	—	—	—	—
$\text{CHPh}=\text{CH}-\text{CH}_2-\text{SBU}^a$	100°/0.05	1.5660	—	—	—	—	—	—
$\text{CHPh}=\text{CH}-\text{CH}_2-\text{SPh}$	(M. p. 77-78°)	—	—	—	—	—	—	—

Allylic Acyclic Sulfides.—These were prepared by treatment of the corresponding allylic chloride or bromide with the sodium salt of the appropriate thiol in alcohol. Where necessary, the chlorides were subjected to high-efficiency fractionation to ensure isomeric homogeneity (tested by infrared spectroscopy). Conditions of halide replacement were chosen to ensure direct (S_N2) substitution. No difficulty was experienced with concomitant alcoholysis. The sulfides were washed with water and then fractionated through high-efficiency columns, and contained no detectable amounts of possible isomers as revealed by their infrared spectra. Their preparation by reaction of a halide with a suspension of the sodium salt of a thiol in benzene or toluene is to be avoided as the sulfide-hydrocarbon azeotropes often obtained on subsequent fractionation are difficult to separate.

The cyclohexenyl and cinnamyl sulfides were kindly provided by F. W. Shipley³ and D. Barnard, respectively.






Physical properties and analyses are recorded in Table 2.

Unsaturated Cyclic Sulfides.—The unsubstituted thiacyclohexenes were prepared by J. Ford according to published procedures; the synthesis of the remaining examples will be described elsewhere³.

Treatment of Sulfides with Alumina.—Immediately before use, the neat sulfides were run through alumina in a silica tube under an atmosphere of oxygen-free nitrogen. The treatment eliminated variable induction periods and minor variations in oxidation rates.

Other Materials.—*n*-Butylcinnamyl sulfoxide, prepared and purified as described by Barnard and Hargrave⁴, had m. p. 66°. Cinnamaldehyde (n_D^{20} 1.6195) and dibutyl disulfide (n_D^{20} 1.4934) were commercial samples purified by

TABLE 3

	B. p./mm.	n_D^{20}		B. p./mm.	n_D^{20}
 (II)	142.5°/758	1.5330	 (IV)	66°/10	1.5280
 (III)	36°/12	1.5346	 (V)	64°/10	1.4932
	50°/10	1.5258			

fractionation. 4-Ethylthiobutan-2-one (n_D^{20} 1.4724) and 3-ethylthiobutanal (n_D^{20} 1.4750) were prepared by addition of ethanethiol to methylvinyl ketone and crotonaldehyde, respectively.

Commercial specimens of quinol (m. p. 170.5°), 2,6-di-*tert*-butyl-*p*-cresol (OH = 1) (m. p. 69.5–70.5°), α -naphthol (m. p. 94.5°), and phenyl- β -naphthylamine (m. p. 107.5°) were recrystallized to constant m. p. $\alpha\alpha'$ -Azoisobutyronitrile was purified by successive precipitations from chloroform solutions with light petroleum. Benzoyl peroxide was purified, first by crystallization from ether, and then by precipitations from chloroform solution with methanol. *tert*-Butyl and cyclohex-2-enyl hydroperoxides were of the purity described by Barnard and Hargrave⁵.

Cobalt stearate was purchased from Messrs. Boake Roberts Ltd., and was used directly. The iron and copper phthalocyanines were highly purified samples, kindly supplied by R. P. Linstead.

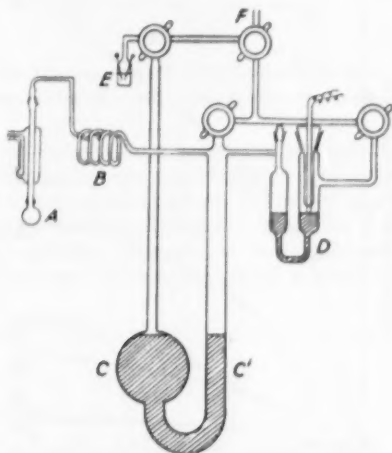


FIG. 1.—Apparatus for measuring oxygen absorption.

A, Silica reaction vessel; B, glass spiral; C, burette with silicone fluid; D, pressure-control device with sodium nitrite in trimethylene glycol as conducting fluid; E, gas generator for pressure equalization; F, outlet to pumps and oxygen supply. A was immersed in a thermostat at the required temperature, the remainder of the apparatus in a tank at $25.00^\circ \pm 0.05^\circ$. Rise in limb C' measured by cathetometer.

Oxidation Procedure.—A constant-pressure type of apparatus was employed as shown in Figure 1. As certain of the cyclic sulfides and those containing the 1,3-dimethylallyl group showed a sensitivity to the nature of the containing vessel and possibly also to mercury vapor, all the measurements now reported were made by using a transparent silica reaction vessel and an involatile silicone as the manometric fluid.

Sulfoxide Estimations.—The oxidized mixtures were analyzed for sulfoxide by Barnard and Hargrave's titanous chloride method⁴.

Peroxide Estimations.—The formation of hydroperoxides in the autoxidizing sulfide was tested by the sensitive ferrous thiocyanate method⁴ and was found to be too small for accurate estimation.

The disappearance of hydroperoxides added to the sulfides as potential catalysts was followed by the stannous chloride method⁴.

RESULTS

General Characteristics.—Most unsaturated sulfides react readily with oxygen at 75°—much more readily initially than a comparable mono-olefin, and somewhat similarly to a 1,4-diolefin (see Figure 2). In contrast to the behavior with olefins, however, a marked retardation develops at an early stage in the reaction, and oxygen absorption often ceases when only a small fraction of a mole of oxygen has been absorbed. Such intense autoinhibition appears to be unique for autooxidations, although a milder form is not uncommon and is associated with the formation of inhibitory substances as a result of decomposition of the primary product. Two processes therefore contribute to the overall oxidation picture: the first, predominating in the earlier stages, is the interaction between the substrate and oxygen; the second, of increasing importance as

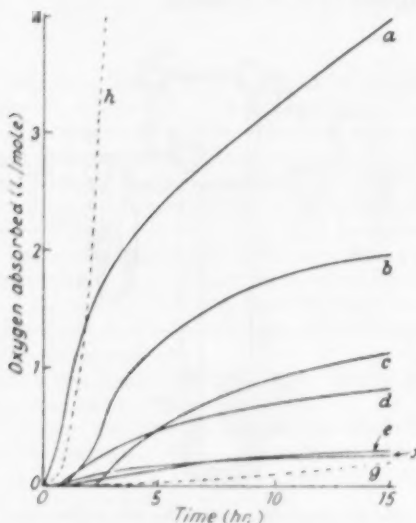


FIG. 2.—Autooxidation of BuSR at 75°.

R = (e) $\text{CHPh:CH}\cdot\text{CH}_2\cdot$, (b) $\text{CHMe:CH}\cdot\text{CHMe}\cdot$, (c) $\text{CH}_2\text{:CH}\cdot\text{CHMe}\cdot$, (d) $\text{CHMe:CH}\cdot\text{CH}_2\cdot$, (f) $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot$. Curves (e), (g), and (A) refer to diallyl sulfide, methyl oleate, and ethyl linoleate, respectively.

reaction proceeds, is the interference caused by the secondary reaction products. Only brief reference will be made to the latter here, since its detailed consideration requires full product analysis (to be reported later); our present concern is mainly with the response of the primary reaction to structural changes and to catalysts and inhibitors.

Reproducibility.—Care being given to synthesis and purification and to the pretreatment with alumina immediately before use, no trouble was experienced with most of the sulfides in obtaining reproducible rates and extents of oxygen absorption. A few cases presented difficulties, however, which are illustrated for the worst example (1,3-dimethylallyl methyl sulfide) in Figure 3. In Pyrex vessels, large variations in the total absorptions were observed, with comparatively minor differences in the initial rates of absorption. The use of silica

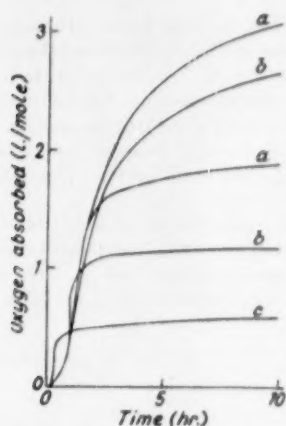


FIG. 3.—Autoxidation of CHMe:CH·CHMe-SMe at 75°.

(a) In silica reaction vessel; (b) in glass reaction vessel; (c) in the presence of powdered glass.

vessels led to a more reproducible but essentially the same initial rate, and reduced, but did not eliminate, the variability in uptake. The addition of powdered glass had a more profound effect, the initial rate being considerably increased and the total uptake being reduced. The glass presumably catalyzes the decomposition of a primary product, so that inhibitors are formed at an earlier stage than otherwise. 1,3-Dimethylallyl *n*-propyl sulfide, but-2-enyl

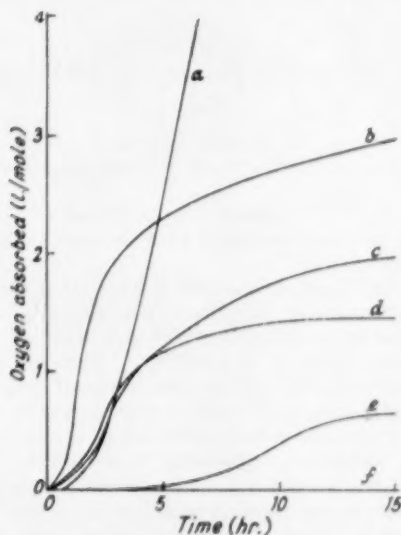


FIG. 4.—Autoxidation of CHMe:CH·CHMe-SR at 75°.

R = (a) Ph, (b) Me, (c) Bu³, (d) Pr³, (e) Pr¹, (f) Bu² (no uptake).

methyl sulfide, and thiacyclohex-2-ene behaved similarly but to a lesser degree; the sensitivity in this respect of the remainder of the sulfides examined was very small. All the results now reported, however, pertain to silica reaction vessels.

Sulfide Structure and Oxidizability.—Saturated sulfides.—The alkyl and phenyl sulfides listed in Table 1 absorbed no oxygen during 24 hours at 75°. More surprisingly (see below), the benzyl- and diphenylmethyl-substituted compounds were found to be similarly inert. The catalyzed oxidation of these sulfides is discussed below.

Acyclic allylic sulfides.—(a) Effect of substitution on the allyl system. Allyl *n*-butyl sulfide and diallyl sulfide react rather slowly with oxygen at 75° and reaction virtually ceases at about 0.3 l./mole (Figure 2). Marked increases in both the rate and extent of absorption occur on progressive substitu-

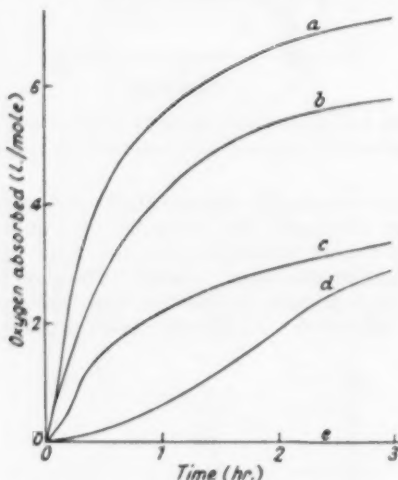


FIG. 5.—Autooxidation of cyclo-C₄H₈SR at 75°.

R = (a) Me, (b) Et, (c) Ph, (d) Prⁱ, (e) Bu^t (no uptake).

tion of methyl and phenyl into the allyl unit (Figure 2). The differences are qualitatively parallel to those associated with analogous substitutional changes in unsaturated hydrocarbons⁷.

(b) Influence of the alkyl substituent in allyl alkyl sulfides. Changes in the saturated or quasi-saturated component in an allyl alkyl sulfide can produce large changes in reactivity, as illustrated for 1,3-dimethylallyl and cyclohexenyl compounds in Figures 4 and 5, respectively. Through the series, methyl, ethyl, isopropyl, *tert.*-butyl, the oxidizability decreases progressively until with the last substituent the compounds behave as though they were saturated i.e., are of negligible reactivity under the experimental conditions. The possibility that the more bulky substituents sterically hinder the approach of reactants to the activated methylene group adjacent to the sulfur atom was shown to be of limited validity by the comparable response of the analogous methyl and *tert.*-butyl compounds to catalysis by azoisobutyronitrile (see Figure 8). It thus appears that the decrease in autooxidizability reflects some intrinsic anti-oxidant activity by the sulfide itself.

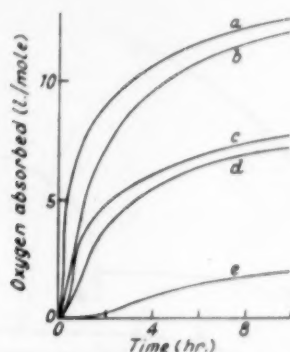
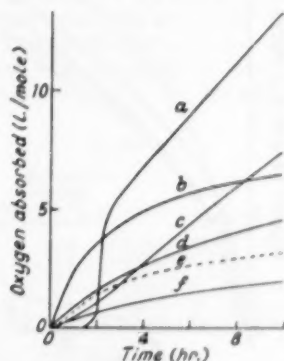


FIG. 6.—Autoxidation of unsaturated cyclic sulfides at 55°.

2-Methyl-5-isopropylthiacyclopent-2-ene. (b) 2-Methylthiacyclohex-2-ene. (c) Thiacyclohex-2-ene. (d) Thiacyclohex-3-ene. (e) 2:3-Dimethylthiacyclohex-2-ene.

Cyclic sulfides.—Compared with comparable acyclic compounds, unsaturated cyclic sulfides are oxidized much more rapidly and show less intense autoinhibition (see Figure 6, which gives absorption characteristics at 55°, not 75°, as for the acyclic sulfides). This is especially so for a substituted thiacyclopentene with vinylic unsaturation.

Catalysts and Inhibitors.—*Effect of different catalyst types.*—The oxidation of *n*-butyl cinnamyl sulfide is promoted by a number of common oxidation catalysts (Figure 7). The important and significant exceptions are benzoyl peroxide, *tert*-butyl hydroperoxide, and cyclohex-2-enyl hydroperoxide. The following experiments show that the catalytic inactivity of the peroxides cannot be attributed to abnormally rapid destruction in the sulfides. (i) *n*-Butyl cinnamyl sulfide (10 ml.), containing *tert*-butyl hydroperoxide (1.1034 g.), was heated at 75° in the presence of oxygen. Samples withdrawn at intervals of 1, 2, and 6 hours after mixing had the following proportions of the original peroxide content present: 46, 28, and 15%, respectively. (ii) The above sulfide


 FIG. 7.—Catalyzed autoxidations of $\text{CHPh}:\text{CH}:\text{CH}_3\text{-SBu}^*$ at 75° (1% by wt. of additive).

(a) Iron phthalocyanine. (b) α,α' -Axiobutyronitrile. (c) Cobalt stearate. (d) Copper phthalocyanine. (e) No catalyst, or cyclohex-2-enyl hydroperoxide or *tert*-butyl hydroperoxide. (f) Benzoyl peroxide.

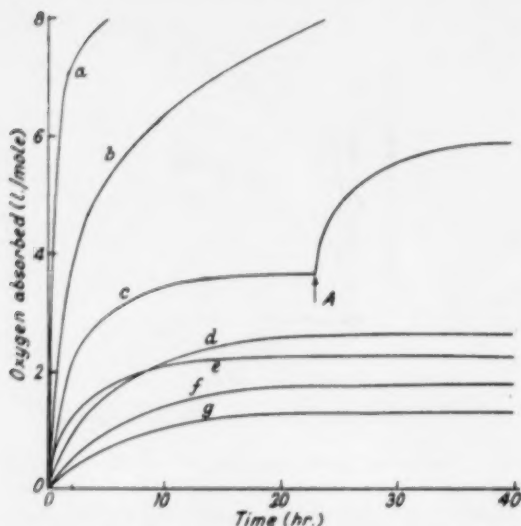


FIG. 8.—Autoxidation of sulfides catalyzed by α' -azoisobutyronitrile (1% by wt.) at 75°.

(a) CycloHex-2-enyl methyl sulfide. (b) $\text{CHPh:CH}\cdot\text{CH}_2\cdot\text{SBu}^s$. (c) $\text{CHMe:CH}\cdot\text{CHMe}\cdot\text{SBMe}$. (d) 2-Ethyl-2-methyl-5-isopropylthiacyclopentane. (e) $\text{CHMe:CH}\cdot\text{CHMe}\cdot\text{SBu}^t$. (f) $\text{Ph}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{Ph}$. (g) MeSBu^s . At A a further 1% of catalyst was added.

(10 ml.), containing benzoyl peroxide (0.5 g.), when heated at 75° for 1 hr. had a peroxide content equal to 10% of the original solution.

Effect of α' -azoisobutyronitrile on different sulfide types.—As shown in Figure 8, azoisobutyronitrile not only promotes the oxidation of unsaturated sulfides but catalyzes the oxidation of otherwise inert saturated types. This is

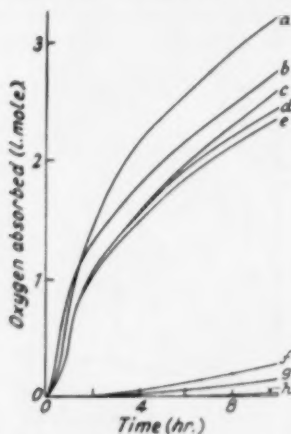
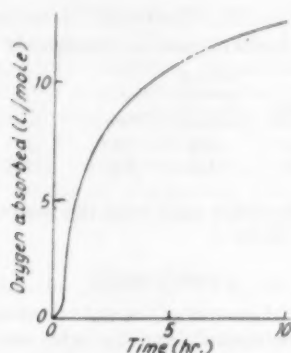


FIG. 9.—Autoxidation of $\text{CHPh:CH}\cdot\text{CH}_2\cdot\text{SBu}^s$ in the presence of various additives at 75° (b—e, 1% by wt.; f—h, 0.1% by wt.).

(a) No addition. (b) $\text{CHPh:CH}\cdot\text{CH}_2\cdot\text{SO}\cdot\text{Bu}^s$. (c) $\text{CHPh:CH}\cdot\text{CHO}$ or Bu^sS_2 or $\text{EtS}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$. (d) H_2O . (e) $\text{EtS}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHO}$. (f) 2:6-Di-*tert*-butyl-*p*-cresol. (g) Phenyl- β -naphthylamine. (h) Quinol or α -naphthol.


 FIG. 10.—Autoxidation of $\text{CHPh:CH}\cdot\text{CH}_2\cdot\text{SPh}$ at 75° .

also true of the unsaturated *tert.*-butyl-substituted sulfides, e.g., $\text{CHMe:CH}\cdot\text{CHMe}\cdot\text{SBu}^t$. Diphenyl sulfide, which has no alkyl-type C—H bonds, provides an exception in not responding to such catalysis. The function of the azo-compound as a chain initiator is strikingly shown in example (c) (Figure 8), where a reaction which stops when the added catalyst has wholly decomposed restarts at almost the same rate on the addition of further catalyst (this has been repeated successively several times).

Photocatalysis.—Irradiation with a mercury-vapor lamp through silica or Pyrex glass increases the rate of oxygen uptake and reduces autoinhibition in those sulfides which autoxidize in the dark. Of those which are inert in the dark, benzyl sulfides, but not dialkyl or diphenyl sulfides, undergo photooxidation.

Inhibitors.—The common amine and phenolic types of oxidation inhibitor strongly retard the autoxidation of *n*-butyl cinnamyl sulfide (Figure 9). 4-Ethylthiobutan-2-one, a type of compound claimed to be an antioxidant for unsaturated natural fats³, and the related 3-ethylthiobutanal exert little effect, as do the major oxidation products of the sulfide viz., *n*-butyl cinnamyl sulf-oxide, cinnamaldehyde, dibutyl disulfide, and water³.

Sulfoxide Formation.—The oxygen uptakes and sulfoxide contents of the various sulfides after reaction with oxygen for 24 hours under the conditions of the absorption measurements recorded in Figures 2, 4, 5, 6, and 10, are shown

TABLE 4



Sulfide	O ₂ absorbed (l./mole)	Sulfoxide content (% of absorbed O ₂)	Sulfide	O ₂ absorbed (l./mole)	Sulfoxide content (% of absorbed O ₂)
$\text{CHPh:CH}\cdot\text{CH}_2\cdot\text{SBu}^s$	4.84	23.9	$\text{CHMe:CH}\cdot\text{CH}_2\cdot\text{SBu}^s$	0.78	5.6
$\text{CHMe:CH}\cdot\text{CHMe}\cdot\text{SBu}^s$	2.33	5.0	$(\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2)_2\text{S}$	0.36	11.8
$\text{CH}_2\cdot\text{CH}\cdot\text{CHMe}\cdot\text{SBu}^s$	1.40	6.6	$\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{SBu}^s$	0.27	23.0
$\text{CHMe:CH}\cdot\text{CHMe}\cdot\text{SPh}$	6.71	5.7	$\text{CHMe:CH}\cdot\text{CHMe}\cdot\text{SBu}^s$	2.33	5.0
$\text{CHMe:CH}\cdot\text{CHMe}\cdot\text{SMe}$	3.18	5.5	$\text{CHMe:CH}\cdot\text{CHMe}\cdot\text{SPr}^i$	0.78	11.0
$\text{CHMe:CH}\cdot\text{CHMe}\cdot\text{SPr}^s$	1.57	5.0	$\text{CHPh:CH}\cdot\text{CH}_2\cdot\text{SPh}$	15.1	9.8
R = 	7.94	13.4	(V)	15.93	17.5
R-SMe	6.40	13.2			
R-SPh	3.93	4.6		13.10	15.0
R-SPr ⁱ	3.83	13.2	(II)	8.90	20.2
			(III)	7.85	52.5
			(IV)	4.52	9.4

TABLE 5

YIELDS OF SULFOXIDE IN AUTOXIDATION OF CYCLOHEX-2-ENYL METHYL SULFIDE

Temp.	Time (hr.)	O ₂ absorbed (l./mole)	Sulfoxide content (% of O ₂ absorbed)	Temp.	Time (hr.)	O ₂ absorbed (l./mole)	Sulfoxide content (% of O ₂ absorbed)
35°	73	6.14	24.8	75°	28	7.94	13.4
55	23	8.74	21.3	95	5.5	4.44	13.5

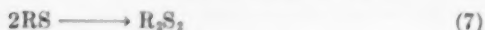
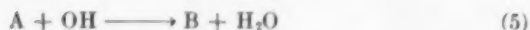
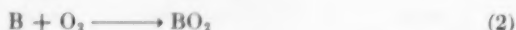
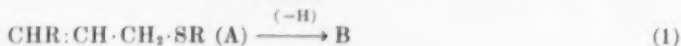
in Table 4. The sulfoxide yields vary with the temperature of oxidation, the trend being illustrated in Table 5.

DISCUSSION

The free-radical chain character of the autoxidations is clearly revealed by the catalysis by azoisobutyronitrile and by light, and the strong retardation by small additions of common oxidation inhibitors. It follows that the remarkable autoretardation and autoinhibition effects must be attributed to specific interference in the chain initiation or propagation steps by one or more of the reaction products. Details of these processes are at present under investigation.

The relative rates of oxidation of a monoolefin, 1:4-diolefin, and an allylic sulfide (see Figure 2) suggest that the doubly activated methylene group is the primary reactive center in the sulfide; cf. $C:C\cdot CH\cdot S$ with $C:C\cdot CH\cdot C:C$. Critical support for this conclusion is afforded by cinnamyl phenyl sulfide, which is autoxidized very readily (Figure 10) and possesses only the above type of potentially active $C-H$ bonds. These considerations discount attack by free radicals at the double bond in the allyl unit (in the primary stage), as does other evidence. First, the effect of substitution in the allyl unit (Figure 2) parallels the relative changes of α -methylenic activity in olefins¹⁰; second, by suitable catalysis, saturated sulfides—with diphenyl sulfide as a significant exception—can be induced to oxidize similarly to their unsaturated counterparts; third, the formation of polymeric products, which would be expected to result if double-bond attack occurred, is inappreciable in allylic sulfides so far examined, but is substantial in the vinylic sulfide, thiacyclohex-2-ene¹¹, where such attack would be expected.

The inhibitory activity of quinol and related substances demonstrates that peroxy- or oxy-free radicals are involved in the propagation step of the autoxidation, and it is therefore reasonable, and consistent with other features such as product composition (cf. following paper) and substitutional effects, to envisage an autoxidation mechanism comprising the following reactions:



where B represents the radical $\text{CHR:CH}\cdot\text{CH}\cdot\text{SR}$, and BO , BO_2 , and BO_2H are the derived radicals and compound. The last would be expected to be highly unstable, of merely transitory existence, decomposing with ease into the aldehyde, water, and disulfide as suggested in reactions (4), (5), (6), and (7).

The formation of sulfoxides as reaction products, sometimes in substantial amount (Table 4), has still to be explained. For this, two supplementary processes are possible. First, since hydroperoxides are known to oxidize sulfides molecularly under conditions comparable with those of autoxidation¹², the unstable compound (BO_2H) may react very rapidly with the substrate according to:



Second, the peroxy-radicals may oxidize the combined sulfur atoms, liberating the oxy-radicals (BO) which can then react as in reaction (10) as well as in (6):



Common to both possibilities is that the hemithioacetal (BOH), rather than BO_2H , is the precursor of the oxidation scission products (see above), which is not unreasonable having regard to our meager knowledge of hemithioacetals¹³.

The significant mechanistic feature introduced by reactions (9) and (10) is the designation of the oxy-radical (BO) as the dehydrogenating chain carrier, and this may well be responsible for certain special characteristics of sulfide autoxidation which are at present difficult to explain. Thus, just as the greater oxidizability of aldehydes compared with olefins seems to reflect the greater reactivity of acylperoxy- compared with alkenylperoxy-radicals¹⁴, the ease of oxidation of unsaturated sulfides may reflect mainly the high reactivity of BO radicals in reaction (10). This in turn is undoubtedly connected with the surprising lack of catalytic activity by peroxides despite the normal behavior of azoisobutyronitrile. It has been shown that this difference cannot be attributed to rapid destruction of the peroxides in the reaction system, and appears to be explicable only in terms of highly specific reactivity of the radicals derived from the various additives. The inactivity of benzoyl peroxide, which is so generally a free-radical catalyst, is puzzling but not unique, for it fails to promote the decarbonylation of aldehydes whereas alkoxy-radicals are effective¹⁵.

SUMMARY

The reactivity of a variety of organic monosulfides towards molecular oxygen has been investigated at temperatures from 45° to 75°. Formally saturated sulfides by themselves are inert, allylic acyclic sulfides react initially much faster than comparable unsaturated hydrocarbons, and allylic and vinylic cyclic sulfides are still more reactive. Oxygen absorption is promoted by light, by the free-radical catalyst $\alpha\alpha'$ -azoisobutyronitrile, and by certain metallic compounds, but not by peroxides. The azo compound is sufficiently active to catalyze the oxidation of saturated sulfides having C—H bonds adjacent to the sulfur atom, while aryl alkyl sulfides also respond to photocatalysis.

A notable feature of these autoxidations is the self-inhibition or strong retardation which generally becomes apparent at small oxygen uptakes.

Certain mechanistic details which can be deduced from the experimental findings are discussed.

ACKNOWLEDGMENT

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IV. AUTOXIDATION OF CYCLOHEX-2-ENYL METHYL SULFIDE

L. BATEMAN AND F. W. SHIPLEY

The autoxidizability of allylic sulfides is characterized by a rapid initial uptake of oxygen, which later falls to a negligible rate when only a fraction of a mole of oxygen has been absorbed¹. One or more of the reaction products must be responsible for this autoinhibition, and this paper describes the first of a series of investigations into what these are and how they act. Cyclohex-2-enyl methyl sulfide (I) was chosen as the first sulfide for detailed study, because it is readily obtained pure (in particular, contamination with allylic isomerides is impossible) and because it absorbs more oxygen before reaction ceases than most other sulfides so far examined.

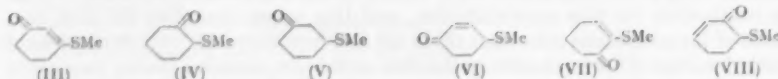


When the sulfide (I) was shaken in oxygen at 55°, it absorbed about 0.3 mole of oxygen per mole before further reaction became negligible. The solution was cloudy and contained water droplets. About a quarter of the absorbed oxygen was combined in sulfoxide groups, as estimated by reduction with titanous chloride².

The reaction mixture was separable by distillation into fractions (i) b. p. 60–70°/14 mm., (ii) b. p. 80–90°/0.1 mm., and (iii) a dark residue involatile at 0.1 mm. Fraction (i) consisted of unchanged sulfide admixed with water, dimethyl disulfide, cyclohex-2-enone, and cyclohex-2-enol. The last two compounds were identified spectroscopically and by the derivatives given with 2,4-dinitrophenylhydrazine and α -naphthyl isocyanate, respectively. Fraction (ii) analyzed approximately for $C_7H_{11}OS$ and had a sulfoxide content about half that of the nearly isomeric cyclohex-2-enyl methyl sulfoxide (II). Fraction (iii), which also had a substantial sulfoxide content, proved to be mainly the decomposition products formed during distillation (see below) and was not examined in detail.

While the infrared spectrum of fraction (ii) and its reaction with 2,4-dinitrophenylhydrazine showed a considerable amount of carbonyl-containing material to be present, attempts at separation by further fractionation proved fruitless. Two other procedures, however, were successful: (a) treatment with titanous chloride reduced the sulfoxide to the original sulfide, which could be distilled from the reduced product to leave a heterogeneous keto-sulfide (KS), b. p. 67–70°/0.1 mm.; (b) chromatography, using silica gel permitted both the sulfoxide (II) and the mixture (KS) to be recovered separately and characterized. Chromatography of the original reaction mixture (after drying) afforded a more thorough, but for sizeable quantities more laborious, overall separation; its application to quantitative estimation of the constituents is described later. Under these mild conditions, the amount of involatile product isolated [fraction (iii) above] was very small.

Composition of the Keto-sulfide (KS).—Elemental analyses and the molecular weight corresponded to the formula $C_7H_{10.7}OS$. Desulfurization with Raney nickel gave cyclohexenal in good yield, thus proving the presence of a cyclic C_6 unit with the oxygen atom attached. The infrared and ultraviolet spectra were complex, but indicated the presence of unconjugated and variously conjugated keto-groups, the simple α,β -unsaturated form being predominant. Weak absorption at 1570 cm^{-1} suggested the presence of about 5 per cent of a triply conjugated chromophore as occurs in (III), and this was consistent with absorption at 1655 cm^{-1} attributed to a highly conjugated ketone group. Ultraviolet absorption at $2900\text{--}3000\text{ \AA}$ was also consistent, but this proved to be non-critical evidence, since differently substituted cyclohexenones were found to absorb similarly (see below).



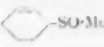


On treatment with 2,4-dinitrophenylhydrazine in aqueous hydrochloric acid, a solid derivative, m. p. $168\text{--}180^\circ$, was obtained in high yield. Non-selective ultraviolet absorption of this product reflected the complexity of the parent ketone. Paper chromatography showed a weak and a strong spot, which had R_F values of 0.38 and 0.19, respectively, under the conditions described. The first of these is attributed to the 2,4-dinitrophenylhydrazone of a saturated keto-sulfide, since the corresponding derivatives of 2- and 3-methylthiocyclohexanone (IV and V) behave similarly; the second is derived from an unsaturated keto-sulfide, but of uncertain type, since the dinitrophenylhydrazones of the differently conjugated 3- and 4-methylthiocyclohex-2-enone (III and VI) have the same R_F value. Fractional crystallization gave a small yield of a derivative of an unidentified saturated keto-sulfide, possibly of 4-methylthiocyclohexanone, since it is not (IV) or (V), which were independently synthesized and characterized, while the major component consisted of dark red needles, m. p. 235° , having an absorption peak in the near ultraviolet at 3750 \AA ($E_{1\text{ cm}}^{1\%}$, 821). These spectral features are intermediate to those shown by the corresponding derivatives of the triply conjugated keto-sulfide (III) (λ_{max} , 2650, 3020, 4000 \AA ; $E_{1\text{ cm}}^{1\%}$, 410, 398, 939) and the unconjugated compound (V) (λ_{max} , 3630 \AA ; $E_{1\text{ cm}}^{1\%}$, 743), and hence were associated with a parent α,β -unsaturated ketone structure. The 2,4-dinitrophenylhydrazone of cyclohexenone absorbs similarly (λ_{max} , 3750 \AA ; $E_{1\text{ cm}}^{1\%}$, 994), and so does the derivative later prepared from (VI) (λ_{max} , 2500, 3740 \AA ; $E_{1\text{ cm}}^{1\%}$, 552, 880), which is otherwise distinguishable from the unknown. Examination of the corresponding semicarbazones led to the same conclusion.

If the double bond is not involved in more than one displacement from its original position in (I), i.e., oxygen attachment is confined to position 1, 2, 3, or 4, the main constituent of (KS) must be either (VII) or (VIII). Reduction with lithium aluminum hydride gave an alcohol which absorbed far less intensely at 2300 \AA than a substituted vinyl sulfide such as would be derived from (VII). Positive identification was finally achieved by the synthesis of (VIII) and direct comparison of the synthetic ketone and its derivatives with the unknown.

Quantitative Estimation of the Products.—The sulfoxide content was determined directly on the oxidized mixture as mentioned above. Dimethyl disulfide was estimated from a separate experiment. The more volatile fraction

of the total oxidation mixture was distilled off and reduced with lithium aluminum hydride, and the resulting thiol estimated by the copper acetate method. Water was determined in a number of separate experiments in which it was distilled from the reaction mixture as its benzene azeotrope and then determined by the Karl Fischer procedure. For the remaining products, the reaction mixture was dried, diluted with light petroleum, and passed through a column of silica gel. After removal of the original sulfide and dimethyl disulfide with successive petroleum washings, the column was eluted with petroleum containing 10–50 per cent of ether to remove cyclohexenone, cyclohexenol, and the keto-sulfides. These components could not be separately determined directly in the mixture, but approximate analysis was possible by separating the first two compounds from the third by distillation and then applying spectroscopic and polarographic methods.

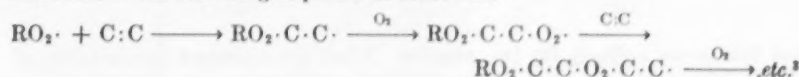
Oxygen Balance.—The approximate distribution of the absorbed oxygen is expressed in the following Table, 93 per cent of the oxygen being accounted for:

	H_2O				(KS)	Residue
Proportion of O_2 absorbed (wt. %) ...	25	23	10	8	22	5

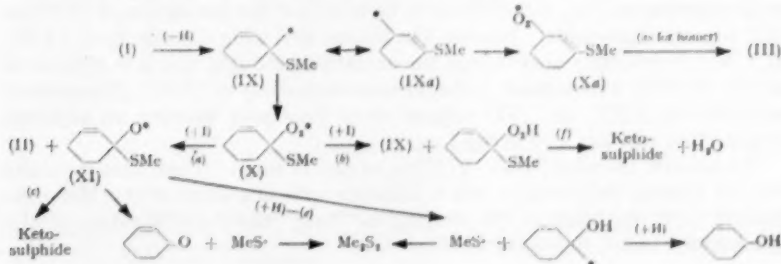
Dimethyl disulfide was formed to the extent of 0.12 mole/mole of oxygen absorbed.

Course of the Reaction.—In view of the complexity of the products and the inference that several alternative or consecutive reactions must be occurring during the oxidation, consideration of the reaction mechanism is limited to developing a reasonable working picture on which to base further experiments.

The general features of the oxidation of allylic sulfides already described¹ lead to two important conclusions. First, the marked catalysis by thermally decomposing azoisobutyronitrile and by ultraviolet irradiation and the inhibition by quinol and similar compounds show that the primary attachment of oxygen involves free-radical intermediates. Second, the fact that oxygen absorption proceeds initially much faster than with a comparable olefin, coupled with the high reactivity of cinnamylphenyl sulfide, points to the CH or CH_2 group activated by both the double bond and the sulfur atom being the primary reactive center. In addition, very little polymeric product is formed, thus showing the unimportance of attack by peroxy-radicals at the double bond and of the following sequence of reactions:



The annexed scheme is based on these features.

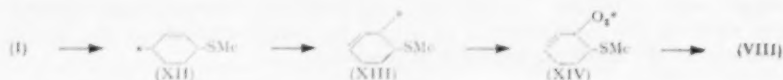


The finding of roughly equal molar proportions of (II), cyclohexenone and cyclohexenol together, keto-sulfide, and water indicates, on this scheme, that reactions (a) and (b) proceed with equal facility and that reaction (c) is negligible. These are not unreasonable consequences.

Hydroperoxides appear to react with allylic sulfides in aprotic solvents, not molecularly as in alcohols to give sulfoxides in quantitative yield, but probably *via* radicals to give only fractional yields of sulfoxides⁴. Hydrogen abstraction by peroxy-radicals, as invoked in step (b), is the fundamental basis of numerous other autoxidations, but the oxygen-transfer process (a) has only recently been recognized⁴. The reactions of (XI) expressed in (d) and (e) simulate the behavior of the formally similar *tert*-alkoxy-radicals derived from *di**tert*-butyl peroxide and *tert*-butyl hydroperoxide⁴. These oxy-radicals show no tendency to oxidize sulfides to sulfoxides in the manner of their peroxy-counterparts⁷.

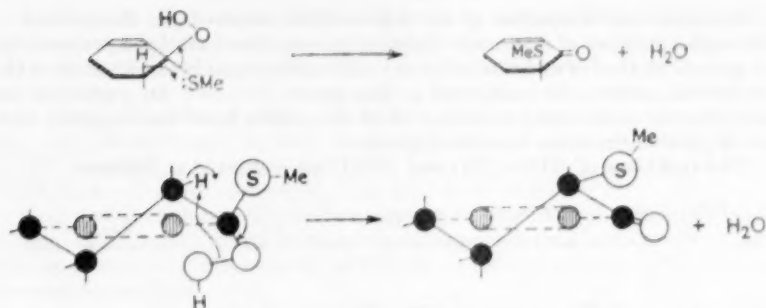
While it is difficult to envisage the transformation of (XI) into a keto-sulfide, the reaction path (IX) \rightarrow (IXa) \rightarrow (Xa) would be expected to give (III). Although spectroscopic evidence points to the presence of (III) in the keto-sulfide mixture, the amount is so small that neither the liquid ketone nor its crystalline derivatives have been separated and characterized. This is a peculiar feature because 1,4-dienes undergo double-bond displacement on autoxidation to give the completely conjugated hydroperoxide⁸: $C:C\cdot CH\cdot C:C \rightarrow C:C\cdot C:C\cdot C(O_2H)$, and similar behavior might have been expected in the present system in view of the considerable conjugation between a double bond and an adjacent sulfur atom⁸, as shown chemically, for example, in the tendency of allylic sulfides to isomerize into vinylic sulfides on heating⁹. Further, whatever the relative importance of the mesomeric structures (IX) and (IXa), steric factors would be expected to cause the latter to be the preferred configuration on reaction with other molecules.

In contrast to the above, a double-bond displacement or an equivalent process is clearly involved in the formation of the main keto-sulfide (VIII). The simplest explanation is that hydrogen abstraction from the sulfide (I) occurs at the non-sulfurated allylic position, followed by reaction of the resulting radical in the isomeric form:



but this seems unlikely for two reasons. First, the increased oxidizability of the cyclohexenyl unit produced by the MeS substituent cannot reasonably be associated with increased reactivity at a methylene group essentially unaffected by the substituent, i.e., it is difficult to believe that the proportion of (XII) to (XI) can be appreciable. Second, the ketone derivable directly from (XII), *viz.*, (VI), is definitely absent from the oxidation products, and it is difficult to see why, if (XII) were formed, it should react exclusively as (XIII) [the spectral properties of (VIII) and (VI) suggest steric hindrance between an adjacent oxygen atom and the MeS group].

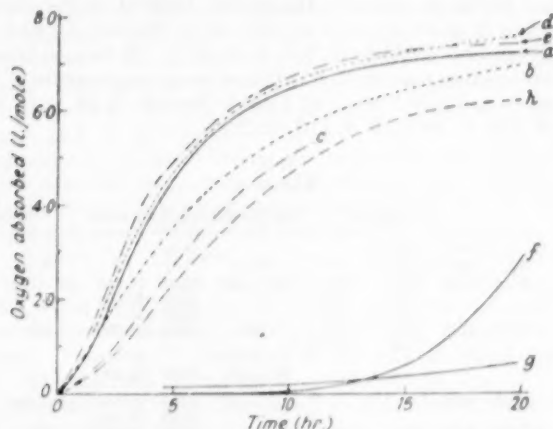
We believe, therefore, that (VIII) is formed in stage (f) and that it results from an internal dehydration which proceeds with migration of the MeS substituent. On the basis of the strained or "half" chair configuration of the cyclohexenyl unit¹⁰, this is pictured as:



Somewhat similar and unusual bond displacements, which scale models show to be quite feasible sterically, are encountered with cyclohexenyl hydroperoxide itself, e.g., in the acid-catalyzed dehydration to cyclopentenylaldehyde.

The chain character of the autoxidation, which is revealed by the response to catalyst and inhibitors (Part III), originates in the operation of reactions (b) and possibly (e).

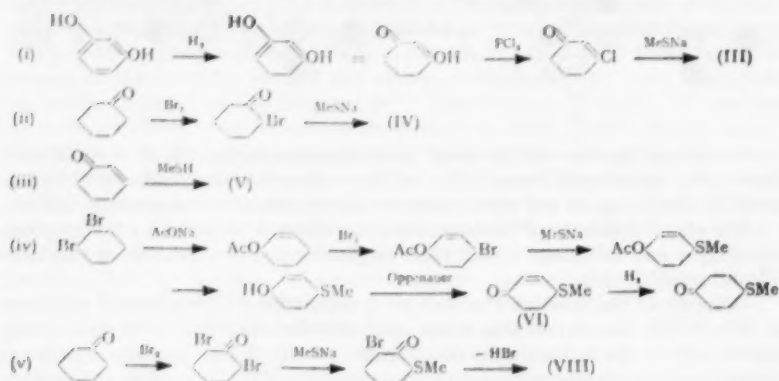
Influence of the Reaction Products on Autoxidation.—The effect of additions of (II), (VIII), cyclohexenone, water, and dimethyl disulfide on oxygen uptake by the sulfide (I) is shown in the Figure. Only (VIII) has any significant effect [which is closely similar to that caused by (III)], and this keto-sulfide acts as a sufficiently powerful retarder to account without difficulty for the observed autoinhibition. Comparison of the action of (VIII), (III), and (IV) reveals the importance of conjugation as a structural feature conferring inhibitory power on compounds of this type. Although certain saturated keto-sulfides are claimed to be efficient antioxidants for natural fats¹¹, the inactivity of (IV) in the present system parallels the small effect of 4-ethylthiobutan-2-one on the oxidation of *n*-butyl cinnamyl sulfide¹.



Effect of the reaction products and some keto-sulfides on the autoxidation of cyclohexenyl methyl sulfide at 55°. a, (I) alone; b, (I) + H₂O (11.8% molar); c, (I) + (II) (4.5% molar); d, (I) + (V) (1.6% molar); e, (I) + cyclohexenone (6.3% molar); f, (I) + (III) (5.4% molar); g, (I) + (VIII) (5.4% molar); h, (I) + dimethyl disulfide (3.2% molar).

Synthesis and Properties of the Keto-sulfides prepared for Comparison.—Although a number of saturated aliphatic keto-sulfides have been prepared by the general method of addition of thiols to α,β -unsaturated ketones¹², most of the homocyclic compounds considered in this paper are new. Of particular interest are the unsaturated examples where the double bond is conjugated with one or both of the other functional groups.

The syntheses of (III)—(VI) and (VIII) were effected as follows:



Certain characteristic properties of these keto-sulfides and their derivatives are summarized in Table I.

EXPERIMENTAL

Microanalyses were carried out under the direction of W. T. Chambers.

CycloHex-2-enyl Methyl Sulfide.—3-Bromocyclohexene¹³ was treated with sodium methyl sulfide in ethanol; the *sulfide*, isolated in the usual way and fractionated, had b. p. 64.5°/14 mm., n_D^{20} 1.5210 (Found: C, 65.5; H, 9.4; S, 25.1. $C_7H_{12}S$ requires C, 65.6; H, 9.4; S, 25.0%). It formed trimethylsulfonium iodide on reaction with methyl iodide at room temperature. The derived sulfoxide¹⁴ had b. p. 75°/0.1 mm., n_D^{20} 1.5384 (Found: C, 58.1; H, 8.5; S, 22.3. Calc. for $C_7H_{12}OS$: C, 58.3; H, 8.4; S, 22.2%).

TABLE I

Compound	n_D^{20}	Keto-sulfide			2,4-Dinitrophenylhydrazone			Semicarbazone		
		ρ_{CO}^1 (cm. ⁻¹)	$\lambda_{max.}$ (\AA)	ϵ^2	M. p.	$\lambda_{max.}$ (\AA)	ϵ^2	M. p.	$\lambda_{max.}$ (\AA)	ϵ^2
(IV)	1.5115	1708	2530 3040 3030	497 315 922*	137—138*	2540 3630 3500 (infl.)	12,310 22,600	171—172°	2300	14,270
(V)	1.5172	1715	2630 2880	339 45.5	148	3630	24,050	165	2310	13,130
p-O: $C_6H_4 \cdot SMe$	—	—	—	—	145—146	3630	22,800	—	—	—
(VI)	1.5487	1690	—	—	146—147	2500 3740	17,780 28,260	156—160	—	—
(VIII)	1.5608	1690	3000	4,250	234	3750	26,700	234	2650	17,440
(III)	1.5902	1655	2870	20,800	212	2650 3020 4000	14,750 12,850 30,250	207—208	2930	34,030

¹ For neat liquids. ² In ethanol, except for * in aqueous 2N-NaOH.

To test the effect of the alkyl substituent on oxidizability¹, the following *cyclohex-2-enyl sulfides* were prepared analogously: *ethyl*, b. p. 76°/14 mm., n_D^{20} 1.5140 (Found: C, 67.5; H, 9.9; S, 22.7. $C_8H_{14}S$ requires C, 67.5; H, 9.9; S, 22.5%); *isopropyl*, b. p. 84°/14 mm., n_D^{20} 1.5062 (Found: C, 68.8; H, 10.4; S, 20.4. $C_9H_{16}S$ requires C, 69.1; H, 10.3; S, 20.5%); *tert.-butyl*, b. p. 97°/14 mm., n_D^{20} 1.5015 (Found: C, 70.5; H, 10.7; S, 18.4. $C_{10}H_{18}S$ requires C, 70.5; H, 10.7; S, 18.8%); *phenyl*, b. p. 77°/0.1 mm., n_D^{20} 1.5929 (Found: C, 75.4; H, 7.2; S, 16.9. $C_{12}H_{14}S$ requires C, 75.8; H, 7.4; S, 16.8%).

Oxidation Procedure.—The sulfide, kept at 55°, was shaken without solvent in purified oxygen supplied from a constant-temperature and -pressure gas-burette, mercury (which behaves as silicone oil for this sulfide¹, being used as the manometric fluid).

Separation of Oxidation Products by Distillation.—The oxidized sulfide (103 g., containing 7.3 g. of oxygen) gave (i) 73 g., b. p. 60–65°/14 mm., n_D^{20} 1.5170, containing unchanged sulfide, water, dimethyl disulfide, cyclohexenol, and cyclohexenone (see below); (ii) 20 g., b. p. 80–90°/0.1 mm., n_D^{20} 1.5435, containing ca. 50% of cyclohexenyl methyl sulfoxide; (iii) 7.6 g., undistillable residue, n_D^{20} 1.5744 (Found: C, 57.4; H, 7.2; S, 20.2; sulfoxide content, by $TiCl_4$, 30%). Redistillation of (ii) gave a fraction (15 g.), b. p. 80°/0.1 mm., n_D^{20} 1.5468 (Found: C, 58.6; H, 8.1; S, 21.2; sulfoxide content, by $TiCl_4$, 49.5%). The mutual volatility of the products prevented more refined separation by distillation, but removal of the sulfoxide from fraction (ii) was effected as follows. A solution in acetic acid (900 ml.) was added with stirring to titanous chloride solution (2430 ml.; 0.1N) containing concentrated hydrochloric acid (150 ml./l.). After being heated at 70–75° for about 2.5 hr., the solution was cooled, set aside overnight, neutralized (ammonium hydroxide), and then extracted for 48 hr. with purified ether. The ethereal extract gave on fractionation: (a) impure cyclohexenyl methyl sulfide (7.0 g.), b. p. 65–67°/14 mm. (Found: S, 22.8%), identified by its infrared spectrum; and (b) a ketonic non-sulfoxylic fraction (8.0 g.), b. p. 67–70°/0.1 mm., n_D^{20} 1.5503 (Found: C, 57.9; H, 7.4; S, 24.3%), henceforth designated (KS).

Reduction of a part of the total oxidation mixture with lithium aluminum hydride gave methanethiol (from dimethyl disulfide) which was distilled off, absorbed in alcoholic sodium hydroxide, and identified as 2,4-dinitrophenyl-methyl sulfide. After several recrystallizations from ethanol this had m. p. 126.5° (Found: C, 39.3; H, 2.8; N, 13.4; S, 14.8. Calc. for $C_7H_4O_4N_2S$: C, 39.3; H, 2.8; N, 13.2; S, 15.0%).

Chromatographic Separation.—Silica gel (200-mesh) was used as adsorbent (decomposition occurred on alumina). All solvents were redistilled immediately before use, the methanol from magnesium methoxide. Oxidized sulfide (11.0 g.) in light petroleum (b. p. <40°; 650 ml.) was passed down the column (45 × 2 cm.), followed by: (1) light petroleum (1250 ml.); (2) light petroleum-10% ether (100 ml.); (3) light petroleum-20% ether (2250 ml.); (4) light petroleum-50% ether (800 ml.); (5) ether (400 ml.); (6) methanol (230 ml.). All eluates were concentrated by carefully evaporating the solvents through a Fenske column. Fraction (1) consisted of the parent sulfide and dimethyl disulfide; (2)–(5) contained cyclohexenol, cyclohexenone, and ketonic sulfides; (6) gave cyclohexenyl methyl sulfoxide, n_D^{20} 1.5374, identified by direct comparison with an authentic specimen¹⁴. Fractions (2)–(5) were combined and fractionated at 0.1 mm. The components volatile at room temperature were cyclohex-2-enol (α -naphthylurethane, m. p. and mixed m. p. with authentic specimen 150–151°) and cyclohex-2-enone (2,4-dinitrophenylhydrazone, m. p.

and mixed m. p. with authentic specimen, 159–160°); the remainder consisted of a fraction virtually identical with (KS), b. p. ca. 70°/0.1 mm., and a small non-distillable residue.

Properties and Characterization of (KS).—(A) Warming with 2,4-dinitrophenylhydrazine in aqueous hydrochloric acid gave a crystalline precipitate, m. p. 168–180°. The heterogeneity of this derivative was clearly shown by paper chromatography (chloroform being used as the stationary phase on acetylated paper), elution by methanol-water (85:15) giving two spots, one weak with R_F 0.38 the other strong with R_F 0.19. The first simulates the behavior of the 2,4-dinitrophenylhydrazones of the saturated keto-sulfides (IV) and (V); the second that of the differently conjugated derivatives from (III) and (VI). Fractional crystallization gave a small proportion of red needles (from pyridine-light petroleum), m. p. 148–149° (Found: C, 48.4; H, 4.8; N, 17.2; S, 9.4. $C_{13}H_{14}O_4N_2S$ requires C, 48.2; H, 5.0; N, 17.3; S, 9.9%), having λ_{max} 3670 Å, $E_{1\%}^{1cm}$ 714; the parent saturated keto-sulfide has not been identified. The main constituent, later shown to be derived from the compound (VIII), formed dark red needles from pyridine-ethanol or benzene, m. p. 235°, λ_{max} 3750 Å, $E_{1\%}^{1cm}$ 787 (Found: C, 48.5; H, 4.4; N, 17.5; S, 9.7. $C_{13}H_{14}O_4N_2S$ requires C, 48.4; H, 4.4; N, 17.4; S, 9.9%).

The semicarbazone of the main constituent of (KS) had m. p. 236°, λ_{max} 2650 Å, $E_{1\%}^{1cm}$ 865 (Found: C, 48.3; H, 6.5; N, 21.1; S, 16.1. $C_8H_{13}ON_3S$ requires C, 48.2; H, 6.6; N, 21.1; S, 16.1%).

(B) The infrared absorption of (KS) indicated the presence of three types of carbonyl grouping: (a) an α,β -unsaturated ketone showing strong absorption at 1690 cm^{-1} ; (b) <5% contained in the more strongly conjugated grouping $S-C=C-C=O$, absorbing at 1656 cm^{-1} ; (c) a minor amount of a saturated ketone absorbing at 1708 cm^{-1} . The ultraviolet spectrum showed broad maximal absorption at 2850–3050 Å ($E_{1\%}^{1cm}$ 290).

(C) The material (KS) (1.2 g.) was heated at 75–80° with Raney nickel¹⁴ (catalyst C) in ethanol solution (50 ml.) with continuous stirring under a stream of nitrogen for 3 hours. The mixture was filtered, the nickel thoroughly extracted with boiling ethanol, and the combined liquors concentrated to about 15 ml. This solution was shaken in hydrogen over palladium-charcoal: no hydrogen was absorbed. The product was isolated in the usual way and distilled (0.7 g.), n_D^{20} 1.4600 (authentic cyclohexanol, n_D^{20} 1.4643). It readily formed an α -naphthylurethane, m. p. and mixed m. p. with a specimen prepared from cyclohexanol, 125–126°. In a trial experiment, 3-methylthiocyclohex-2-enone (III) gave cyclohexanol in similar yield.

(D) Hydrogenation of (KS) over palladium-charcoal (hydrogen absorption, 0.85 mole), and distillation gave a product consisting largely of 2-methylthiocyclohexanone (IV), n_D^{20} 1.5200, and having an infrared spectrum nearly identical with that of a synthetic specimen. This compound was definitely absent before hydrogenation. The orange 2,4-dinitrophenylhydrazone could not be obtained pure by crystallization, and had a m. p. several degrees lower than the derivative prepared from the synthetic keto-sulfide.

(E) Reduction of (KS) (0.6 g.) with lithium aluminum hydride (0.1 g.) in dry ether (10 ml.), and isolation of the product in the usual way, gave a liquid (0.35 g.), n_D^{20} 1.5650 (Found: C, 56.5; H, 7.7; S, 24.4%). The small amount of (III) originally present appeared to remain unreduced as shown by the non-disappearance of bands at 1655 and 1570 cm^{-1} , but the absence of absorption at 1690 cm^{-1} (due to unsaturated carbonyl grouping) showed that reduction

of the main constituent was complete. The ultraviolet spectrum was consistent with the latter conclusion (weak absorption at 2900 Å), the relatively weak absorption at 2300 Å proving the absence of vinylic sulfide grouping $C=C-S$. There is very strong absorption in the 3- μ region. The compound is impure 6-methylthiocyclohex-2-enol.

Synthesis of 6-Methylthiocyclohex-2-enone (VIII) and its Identification as the Main Component of (KS).—Methyl sodium sulfide solution prepared from sodium (4.0 g.) and excess of methanethiol was added very slowly with vigorous stirring to 2,6-dibromocyclohexanone¹⁸ (46 g., m. p. 107°) in dry methanol at room temperature. After the addition was complete, the solution was warmed to 50° for 1 hour, then concentrated under reduced pressure, the sodium bromide filtered off, and finally the solvent removed. Attempts to distil the residue led to its decomposition. The crude material was therefore debrominated by treatment with potassium hydroxide (9.0 g.) in ethanol (90 ml.), first at room temperature (3 hr.), then by warming to the b. p. The solution was cooled and filtered, and the solvent removed under reduced pressure. Fractionation of the residue gave 6-methylthiocyclohex-2-enone (15 g.), b. p. 76–78°/

TABLE 2

	KS:		(VIII)
	Bulk	Main component	
n_D^{20}	1.5503	—	1.5608
λ_{max} , $E_1^{1\%}$ cm.	2850–3050 Å, 290	—	3600 Å, 299
Carbonyl absorption (cm. ⁻¹)	1690, 1655, 1708	—	1690
2:4-Dinitrophenylhydrazones { m. p. λ_{max} , $E_1^{1\%}$ cm.	168–180°	235°	234°
	3700 Å, 719	3750 Å, 831	3750 Å, 829
Semicarbazones { m. p. λ_{max} , $E_1^{1\%}$ cm.	219–222°	236°	234°
	2650 Å, 815	2650 Å, 865	2650 Å, 877

0.1 mm., n_D^{20} 1.5608 (Found: C, 58.9; H, 7.1; S, 22.0. $C_7H_{10}OS$ requires C, 59.1; H, 7.1; S, 22.5%). The 2,4-dinitrophenylhydrazone, recrystallized from pyridine-ethanol and benzene, formed dark red needles, m. p. 234° (Found: C, 48.3; H, 4.4; N, 17.0; S, 9.7. $C_{13}H_{14}O_4N_4S$ requires C, 48.4; H, 4.4; N, 17.4; S, 10.0%). The semicarbazone had m. p. 234° (Found: C, 48.1; H, 6.6; N, 21.1; S, 16.1. $C_8H_{13}ON_3S$ requires C, 48.2; H, 6.6; N, 21.1; S, 16.1%).

The properties of (KS) and (VIII) are compared in Table 2.

Quantitative Estimation of Oxidation Products.—(A) *Sulfoxide.*—This was estimated directly on the total oxidation mixture by Barnard and Hargrave's method², and was always within close limits, viz., 23–25% of the oxygen absorbed.

(B) *Water.*—This was also estimated on the total oxidation mixture by Karl Fischer's procedure, the usual rigorous precautions to exclude the intrusion of extraneous moisture being observed. The oxidized mixture was washed from the oxidation vessel into a distillation flask with methanol (2–4 ml.) followed by benzene (30–40 ml.). The water-benzene azeotrope was distilled off through a twisted gauze column with a head designed to minimize condensation, and collected in a cooled receiver. The water in the distillate was estimated by electrometric titration with the usual reagents¹⁷. Blank titrations were performed on the solvents. Control experiments with unoxidized sulfide, sulfoxide (dried by azeotropic removal of water with benzene), and a weighed

amount of water gave results consistently high by 3.6 mg. after allowance for the solvent blank. Results:

O ₂ absorbed (mole/mole)	0.28	0.35	0.34	0.32	0.16	0.16
H ₂ O (mg.) (corr.)	7.8	11.8	11.0	6.5	5.7	7.3
Absorbed O ₂ found as water (wt. %)	18.7	25.6	25.8	18.0	25.1	30.7

(C) *Dimethyl disulfide*.—This was estimated (a) by reduction to the thiol and (b) polarographically. (a) Fraction (i) of the total oxidation mixture in tetrahydrofuran was dried and reduced with excess of lithium aluminum hydride in ether. Careful addition of cold ethanol and 2*N*-sulfuric acid gave methanethiol, which was estimated by passage into standard cupric acetate solution, the excess of cupric salt being measured iodometrically¹⁸. Sulfide (5.55 g.) containing oxygen (0.26 mole/mole) gave dimethyl disulfide (0.14 g.). (b) Polarographic estimation on the total oxidation mixture was impossible owing to interference by the relatively large amount of sulfoxide. A polarogram of the fraction used in (a) in 85% acetone-free methanol-15% water containing 0.1 *M*-lithium chloride at a dropping-mercury cathode gave a wave of height equal to the sum of those due to dimethyl disulfide and cyclohexenone. The wave height, obtained by subtraction of that due to cyclohexenone [see D (b)], corresponded to dimethyl disulfide (0.12 g.).

Estimation of the remaining products was carried out on the appropriate fraction from the chromatographic separation described above, the cyclohexenone and cyclohexenol being contained in the more volatile part of the fractions (2)–(5).

(D) *Cyclohex-2-enone*.—This was estimated (a) spectroscopically and (b) polarographically. (a) Comparison of intensity of absorption at 1688 cm.⁻¹ (conjugated carbonyl) with that of the pure ketone gave a content of 0.29 g., representing 10.3% of the total oxygen absorbed. (b) Comparison of the wave, given in 85% acetone-free methanol-15% water containing an acid buffer (HCl and NaOAc) with that of the pure ketone gave a cyclohex-2-enone content of 0.28 g., representing 9.8% of the total oxygen absorbed. Polarographic estimation directly on the more volatile part of the total oxidation mixture [fraction (i),] gave a value of 8.2% of the total oxygen absorbed.

(E) *Cyclohex-2-enol*.—Estimation of the intensity of the OH stretching frequency in the 3- μ region gave an approximate value of 0.22 g., representing 7.9% of the total oxygen absorbed.

(F) *Keto-sulfide*.—Infrared and ultraviolet examination showed this fraction to have an almost identical composition with that of fraction KS, accounting for 22% of the total oxygen absorbed.

(G) *Involatile residue* (0.14 g.) not identified (Found: O, by diff., 15%), corresponding to 4.5% of the total oxygen absorbed.

Syntheses of Keto-sulfides.—(1) *2-Methylthiocyclohexanone* (IV).—Crude 2-bromocyclohexanone (12.5 g.; b. p. 55–60°/0.1 mm.) (Found: Br, 43.7. Calc. for C₆H₉OBr: Br, 45.1%), prepared by Kötze's method¹⁹, in ether (20 ml.) was added slowly, with stirring, to a solution of methyl sodium sulfide (from 1.64 g. of sodium) in methanol (30 ml.) at 0°. After being warmed to room temperature, the mixture was refluxed for a few minutes, and then worked up in the usual way. The required *keto-sulfide* (3 g.) had b. p. 51°(0.1 mm.), n_D^{20} 1.5115 (Found: C, 57.5; H, 8.2; S, 21.8. C₇H₁₁OS requires C, 58.3; H, 8.4; S, 22.2%).

(2) *3-Methylthiocyclohexanone* (V).—*Cyclohex-2-enone* (5.0 g., prepared by oxidation of *cyclohexene* with chromic anhydride²⁰, piperidine (0.5 g.), and dry benzene (20 ml.) were mixed in a Carius tube into which methanethiol (3.5 ml.) was then distilled. After being sealed, the tube was heated at 55° for 5 hr. Fractionation of the product gave *3-methylthiocyclohexanone* (V) (4.5 g.), b. p. 55°/0.1 mm., n_D^{20} 1.5172 (Found: C, 58.7; H, 8.5; S, 21.7. $C_7H_{12}OS$ requires C, 58.3; H, 8.4; S, 22.2%).

(3) *4-Methylthiocyclohex-2-enone* (VI).—1-Acetoxy-4-bromocyclohex-2-ene¹³ (65.7 g.) in ethanol (100 ml.) was added slowly to a solution of methyl sodium sulfide (from 6.9 g. of sodium) at room temperature. The mixture was refluxed for 30 min., most of the alcohol then distilled off, and 1-acetoxy-4-methylthiocyclohex-2-ene (46 g.), b. p. 67°/0.1 mm., n_D^{20} 1.5375, isolated in the usual manner. Hydrolysis of this compound with sodium hydroxide in ethanol gave *4-methylthiocyclohex-2-enol* (28 g.), b. p. 65–67°/0.1 mm., n_D^{20} 1.5468 (Found: C, 58.2; H, 8.2; S, 22.1. $C_7H_{12}OS$ requires C, 58.3; H, 8.4; S, 22.2%), which on Oppenauer oxidation and careful fractionation of the product gave *4-methylthiocyclohex-2-enone* (4.0 g.), b. p. 69°/0.1 mm., n_D^{20} 1.5489 (Found: C, 59.2; H, 7.3; S, 22.6. $C_7H_{10}OS$ requires C, 59.1; H, 7.1; S, 22.5%).

Hydrogenation of this keto-sulfide over palladium-charcoal gave impure 4-methylthiocyclohexanone, which formed an orange-yellow 2,4-dinitrophenylhydrazone (from light petroleum-ethanol), m. p. 145–146° (Found: C, 48.3; H, 5.2; N, 17.1. $C_{12}H_{16}O_4N_4S$ requires C, 48.2; H, 5.0; N, 17.3%).

(4) *3-Methylthiocyclohex-2-enone* (III).—Dihydroresorcinol, m. p. 98°, obtained by hydrogenation of resorcinol over Raney nickel²¹ was converted into *3-chlorocyclohex-2-enone* (b. p. 78°/14 mm., n_D^{20} 1.5204. Found: Cl, 27.2. Calc. for C_6H_7OCl : C, 55.2; H, 5.4; Cl, 27.2%) by treatment with phosphorus trichloride in chloroform²². This chloro-compound (8.2 g.) in benzene (10 ml.) was added to a suspension of methyl sodium sulfide in benzene (obtained by saturating methanol containing sodium with methanethiol and then changing the solvent by distillation and simultaneous addition of benzene) at 0° with vigorous stirring. After 1 hr., the mixture was heated to 70–80° for 0.5 hr., cooled, and poured into water. Ether-extraction and subsequent fractionation gave *3-methylthiocyclohex-2-enone* (5.0 g.), b. p. 75°/0.1 mm., n_D^{20} 1.5902 (Found: C, 59.0; H, 7.0; S, 22.4. $C_7H_{10}OS$ requires C, 59.1; H, 7.1; S, 22.5%).

SUMMARY

Cyclohex-2-enyl methyl sulfide readily absorbs up to about 0.3 mole of oxygen per mole at 55° to yield a complex mixture. Cyclohexenyl methyl sulfoxide, 6-methylthiocyclohex-2-enone (VIII), cyclohexenone, cyclohexenol, water, and dimethyl disulfide have been identified and estimated approximately quantitatively. A reaction mechanism consistent with these and other experimental data is presented and discussed.

Several new keto-sulfides which were required as reference compounds have been prepared and characterized; the sulfide (VIII) and its 3-methylthio-isomer (III) show marked antioxidant activity.

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TEMPERATURES OF VITRIFICATION AND FLUIDITY OF NATURAL RUBBER OF DIFFERENT MOLECULAR WEIGHTS *

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As is known, amorphous high molecular compounds at various temperatures can occur in three physical states: vitreous, high-elastic, and viscous fluid. Kargin and his collaborators studied the transition from one physical state to another for various polymers as related to the molecular weight. Kargin and Sogolova¹ showed that for one elastic polymer—polyisobutylene—the following law is observed: the vitrification temperature in the range of molecular weights from 6000 to 3,500,000 does not depend on the molecular weight and maintains a constant value, equal to -65°C , while the fluidity temperature rises as the value of the molecular weight increases.

We thought it interesting to study the behavior of natural rubbers of various molecular weights during a change in temperature over a wide range. This is doubly important, because one of the necessary stages of technological process in the manufacture of natural rubber goods is plasticization, as a result of which rubbers of varying molecular weights are obtained.

EXPERIMENTAL PART

Natural smoked-sheet rubber and a rubber prepared by the factory method from kok-saghyz were chosen for this study.

In order to obtain rubbers of varying molecular weights, the specimens were plasticized on a laboratory mill for varying periods. For smoked sheet, the plasticization times were 5, 10, 15, and 20 minutes; for kok-saghyz, 5 and 10 minutes. The molecular weights of the rubbers were determined by measuring the viscosity of their solutions in benzene. The soluble part of the rubber was separated and then the rubber was precipitated from solution with ethyl alcohol and dried, and from it were prepared solutions for determining the viscosity and specimens for the thermomechanical curves. The viscosity was measured in an Ostwald viscometer. The temperature of the measurements was $25 \pm 0.1^{\circ}\text{C}$. The values of the specific and reduced viscosities were calculated from the measurements of relative viscosity of four concentrations; the values of the characteristic viscosities were obtained graphically.

In Figure 1 are shown the results obtained for smoked sheet, and in Figure 2, for kok-saghyz. As is seen from the figures, the rubber specimens differ considerably from one another in the values of the characteristic viscosities, while the higher the characteristic viscosity is, the steeper is the slope of the curves. The latter law was observed by various authors for solutions of different polymers, particularly solutions of butadiene rubbers².

On the basis of these data, we calculated the molecular weights for smoked sheet, using the equation: $[\eta] = K \cdot M^a$ and the values of the constants K and

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α , taken for natural rubber-toluene systems². The data obtained are shown in the table.

For all the specimens prepared, we studied the relation of the deformation to the temperature on a Kargin dynamometer¹. The working load was 50 g. per sq. cm. The curves for smoked-sheet specimens of varying molecular weight are shown in Figure 3, and those for kok-saghyz in Figure 4.

From these values it follows that the laws established by Kargin and Sogolova for polyisobutylenes apply also to natural rubbers.

The vitrification temperature does not depend on the value of the molecular weight; that is, the extent of destruction during plasticization has no influence

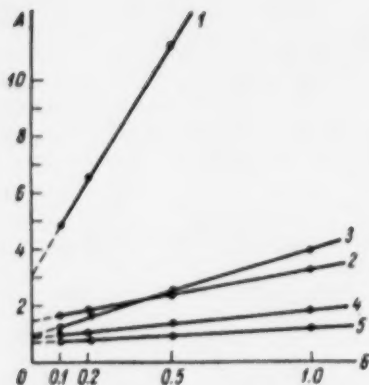


FIG. 1.—Relation of reduced viscosity to concentration for smoked-sheet rubber. A.—reduced viscosity. B.—concentration (in g./100 ml.). Molecular weight: 1—427000; 2—152000; 3—96000; 4—71000; 5—49000.

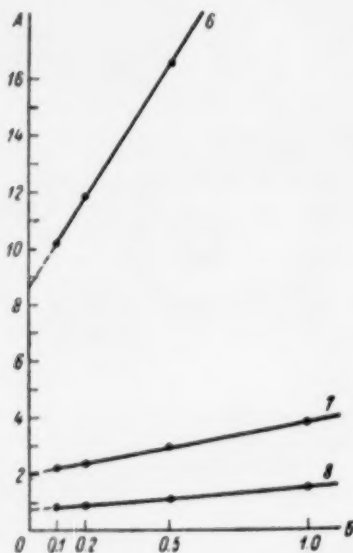


FIG. 2.—Relation of reduced viscosity to concentration for kok-saghyz rubber. A.—reduced viscosity. B.—concentration (in g./100 ml.). Molecular weight: 6—specimen c [η] = 8.6; 7—[η] = 2.0; 8—[η] = 0.7.

on the vitrification temperature of natural rubber. The fluidity temperature T_T is strongly influenced by the value of the molecular weight.

Thus: specimen 1 ($M = 427,000$) has $T_T = 140^\circ \text{C}$, specimen 2 ($M = 152,000$) has $T_T = 60^\circ \text{C}$, specimen 3 ($M = 96,000$) has $T_T = 35^\circ \text{C}$, specimen 4 ($M = 71,000$) has $T_T = 30^\circ \text{C}$, and specimen 5 ($M = 49,000$) has $T_T = 10^\circ \text{C}$.

For unplasticized kok-saghyz, $T_T = 90^\circ \text{C}$; for the specimen with characteristic viscosity [η] = 2.0, $T_T = 50^\circ \text{C}$, for the specimen with [η] = 0.7, $T_T = -20^\circ \text{C}$.

The original smoked sheet possesses high elasticity in the temperature range from 70° to 140° , and the original kok-saghyz in the range from -60° to 90°C . The value of the square of high elasticity decreases with decrease in the molecular weight. Thus, rubber of molecular weight 49,000 at room tempera-

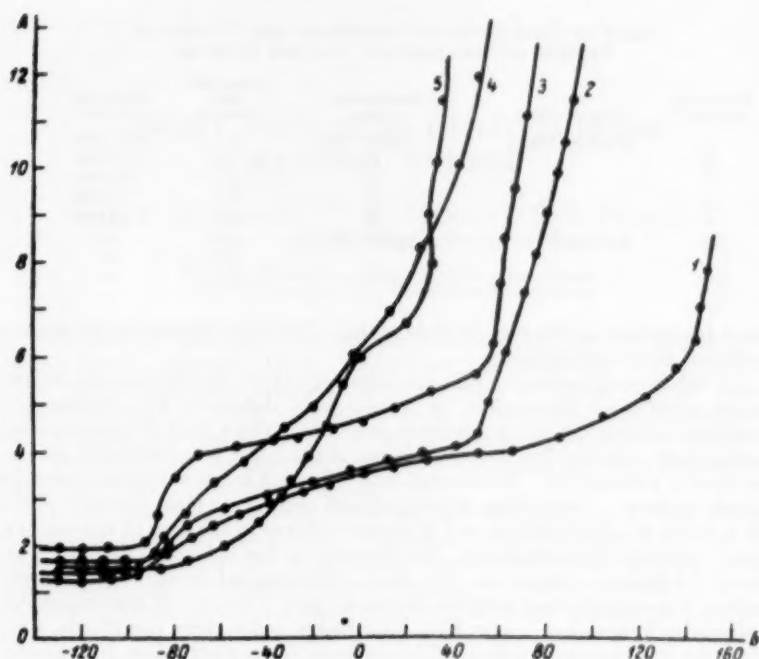


Fig. 3.—Relation of deformation to temperature for smoked-sheet rubbers. A.—deformation in units of the scale; B.—temperature in $^{\circ}\text{C}$. Molecular weight: 1—427,000; 2—152,000; 3—96,000; 4—71,000; 5—49,000.

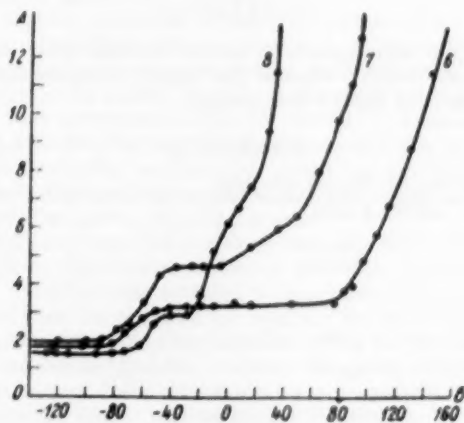


Fig. 4.—Relation of deformation of temperature for kok-saghyz rubbers. A.—deformation in units of the scale; B.—temperature in $^{\circ}\text{C}$. 6—specimen $[\eta] = 8.6$; 7— $[\eta] = 2.0$; 8— $[\eta] = 0.7$.

VALUE OF CHARACTERISTIC VISCOSITIES AND MOLECULAR WEIGHTS OF SPECIMENS OF NATURAL RUBBERS

Number of specimen	Type of rubber	Plasticization time	Characteristic viscosity	Molecular weight
1	Smoked Sheet	Unplasticized	3	427,000
2		5	1.5	152,000
3		10	1.1	96,000
4		15	0.9	71,000
5		20	0.7	49,000
6	Kok-saghyz	Unplasticized	8.6	—
7		5	2.0	—
8		10	0.7	—

ture is practically in the viscous-fluid state. The same occurs in kok-saghyz plasticized for 10 minutes.

It is interesting to observe that the behavior of two types of natural rubber, smoked sheet and kok-saghyz, is considerably different: the original unplasticized kok-saghyz has a viscosity more than twice that of unplasticized smoked sheet, and the fluidity temperature of the latter is considerably greater than that of kok-saghyz. This attests to a difference in the molecular structure of these rubbers. Destruction of both rubbers takes place most intensely in the first minutes of plasticization, and it is more intense in the case of kok-saghyz. After 5 minutes of plasticization, the viscosity of the kok-saghyz solution decreased 3.5 times in comparison with that of the original rubber, while the viscosity of the smoked sheet solution decreased only 2 times. It was impossible to plasticize kok-saghyz longer than 10 minutes under these conditions, since it became completely liquefied. This propensity to destruction is evidently explained by the fact that domestic kok-saghyz is distinguished by a high content of iron and manganese, which are positive oxidation catalysts.

The relation of the fluidity temperature to the molecular weight of natural rubbers must be taken into consideration by technologists in the development of systems of processing rubber and preparing rubber articles.

CONCLUSIONS

The vitrification temperature of natural rubbers does not change with change of molecular weight, whereas the higher the molecular weight of the rubber, the higher is its fluidity temperature.

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GRAFT POLYMERS DERIVED FROM NATURAL RUBBER *

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Conventional methods for reinforcing natural rubber involve the addition of carbon black or inorganic fillers. More recent developments in reinforcement have utilized polymeric resinous materials, such as lignin, cyclized rubber, phenolic resins, and vinyl polymers in finely divided form, and the degree of reinforcement obtained appears to be very dependent on the degree of dispersion and physical form of the dispersed particles as effected by mixing or coprecipitating rubber with the reinforcing agent.

An alternative technique involves the chemical grafting of vinyl polymer side-chains on to natural rubber. This should have a dual effect: first, the attached side-chains should be coiled and hence simulate the function of particulate fillers, and, being polymeric in character, might be expected to improve the fatigue properties without loss of elasticity; secondly, there is the possibility of control of the elastic properties of the product by variation in the polarity, flexibility, and chemical reactivity of the attached side chains.

Among the earliest recorded attempts to modify rubber by polymerization of monomers dissolved in rubber or dispersed in latex were those sponsored by the Rubber Growers' Association¹. Later, Compagnon and Le Bras² described polymerization of acrylonitrile and other vinyl monomers in deammoniated rubber latex, with the aid of rather substantial amounts of ethyl hydroperoxide, benzoyl peroxide, or persulfates. In some instances the solubility of the product was quite different from that of either the rubber or the polymer or mixtures of the two. Persulfate initiators appear to be less sensitive to ammonia than benzoyl peroxide, and some interesting modifications of rubber by polymers, and of polymers by rubber, have been described in the patent literature³. Working under very considerable difficulty during the Japanese occupation of Java, Koolhaas, van der Bie, and van Essen⁴ succeeded in showing that some vinyl monomers (including acrylonitrile, methyl methacrylate, and styrene) could be polymerized after their addition to rubber latex, although ammonia was again observed to have a retarding action.

In none of the foregoing work has there been any clearcut evidence of combination of polymer with rubber, either by polymeric interaction or by graft polymerization. Nor have the modified rubbers been systematically evaluated.

In the present work the emphasis has been laid in the first place on establishing that combination does take place between rubber and the vinyl polymer and in determining the number and the length of the grafted chains. In addition, the aim has been to graft these side-chains on to the rubber by methods which could be controlled by known polymerization techniques.

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TRANSFER MECHANISMS IN THE FORMATION OF GRAFT POLYMERS

Rubber contains labile α -methylenic hydrogen atoms, which should be prone to capture by a growing vinyl polymer chain, which would thus be converted into a polymer molecule, while a free radical center would be created on the rubber molecule. From this center a new polymer chain should grow. Such transfer reactions have been studied extensively with vinyl monomers and ordinary transfer agents, such as isopropylbenzene, which contains an α -methylenic hydrogen atom, and carbon tetrachloride which has a labile halogen atom. It is well known that the molecular weight of the vinyl polymer due to early termination by the transfer agent obeys the relation:

$$\frac{1}{P} = \frac{1}{P_0} + C \cdot \frac{(S)}{(M)} \quad (1)$$

where P_0 is the chain length in the absence of transfer agent, and P is the chain length when there is a molar ratio $(S)/(M)$ of transfer agent to monomer. C is the transfer coefficient, and it expresses the frequency with which transfer occurs relative to the ordinary growth of the polymer chain. In the case of normal transfer agents, the polymer chains initiated by catalyst or from the transfer agent are indistinguishable and inseparable. But when a macromolecular transfer agent is used, the chains initiated from the catalyst in the first step of the reaction will be free unattached vinyl polymer, whereas those initiated as a result of the transfer reaction will be attached to the rubber. The ratio R of bound polymer to free polymer is given by the relation:

$$R = P_0 \cdot C \cdot (S)/(M) \quad (2)$$

The magnitude of C , the transfer coefficient, is a major factor in determining both P and R , and experiments were first made with a model polyisoprenic hydrocarbon dihydromyrcene (DHM), in which the α -methylenic groups have a similar chemical reactivity to those in rubber. These experiments⁵ gave the following values for C .

Monomer	Transfer coefficient
Styrene	2×10^{-4}
Methyl methacrylate	7×10^{-4}
Acrylate	4×10^{-3}
Vinyl acetate	4×10^{-2}

From Equations (1) and (2) it can be seen that styrene should give a small number of long chains, the ratio of attached to free polymer being small, whereas with vinyl acetate there should be a large number of small chains grafted to the rubber, with only a small amount of unattached vinyl polymer. Examination of these differences has been impeded by the fact that both DHM and rubber severely retard the polymerization of vinyl acetate. For this reason, and also because it was believed that longer side-chains would give a more readily detectable pattern of combination with rubber, the methyl methacrylate and styrene systems have been studied more.

GRAFT POLYMERS BASED ON METHYL METHACRYLATE AND STYRENE

When the interaction of rubber and methyl methacrylate was studied in solution, it was found that, using benzoyl peroxide as catalyst, combination did

take place, but that the attached polymer chains were very much shorter and more numerous than the unattached chains⁶. The proof of this condition depended on a rigid separation of the three possible components of the reaction, viz., rubber, rubber-vinyl polymer compound, and free vinyl polymer.

The separation was made by adding methyl alcohol to a 1 per cent solution in benzene of the "gross" polymer. All the free rubber precipitated after 25 per cent of alcohol (on the volume of original solution) had been added. Subsequent addition of alcohol caused the formation of a very stable sol, the particles of which apparently consisted of a collapsed rubber chain, kept in Brownian movement by the continued solubility of the vinyl polymer side-chains. The extraordinary stability of this sol, which does not coagulate on boiling or on treatment with large concentrations of ionic substances, such as calcium chloride, testified to the marked degree to which the rubber had been modified. When about 180 per cent of methyl alcohol had been added, the sol flocculated (aided by the presence of a minute trace of calcium chloride), presumably owing to collapse of the side-chains. After a certain further addition of methyl alcohol, the free vinyl polymer started to separate; there was always a reasonable gap between flocculation of the sol and the precipitation of the free vinyl polymer. Critical checks of this separative procedure showed that effective separation had taken place, and confirmed that the middle fraction was undoubtedly the rubber-polymer compound alone. A suitable modification to the solvent mixture enabled the method to be applied to styrene-modified rubber.

The relative amounts and molecular weights of the three fractions present showed that, while the free vinyl polymers reached their expected molecular weight in the range 200,000 to 500,000, the attached chains had a molecular weight as low as 2000, that is, about 20 monomer units. This statement was true of both methyl methacrylate and styrene, despite their different transfer coefficients. The amount of bound vinyl polymer, despite the shortness of the chains, was somewhat greater than that calculated from the transfer theory.

INFLUENCE OF INITIATOR ON COURSE OF POLYMERIZATION

The efficiency of benzoyl peroxide is known to vary with environment, owing to complicated side reactions; therefore the above experiments were repeated, using azoisobutyronitrile (AZBN), whose decomposition is known to be insensitive to environment. The results showed that very little vinyl polymer was attached to the rubber; 95 per cent or more of the monomer polymerized gave free polymethyl methacrylate or polystyrene of the usual high molecular weight.

This difference in behavior of systems initiated with peroxides and AZBN can be demonstrated visually. If methyl methacrylate containing 10 to 20 per cent of dissolved rubber is polymerized in bulk with benzoyl peroxide, a tough translucent polymer is obtained. With AZBN, the product is an opaque brittle mass, demonstrating the poor mutual solubility of rubber and free vinyl polymer.

Thus neither the results with benzoyl peroxide nor with AZBN as catalyst correspond with those predicted by the transfer theory. It is not possible to say whether the large number of attached chains produced is due to direct attack on the rubber by peroxidic catalysts or to a higher transfer rate as soon as the first transfer act with the rubber has occurred. The former is unlikely because of the very great increase of the number of required initiating points,

and the latter is complicated because the experimental results show clearly that the graft side-chains are spread evenly among all the rubber molecules. The failure of AZBN to produce graft polymer, while allowing polymerization of the monomer to proceed to high yields independently of the rubber, would appear to eliminate transfer as the operative step in the formation of graft polymers.

GRAFT POLYMERS FROM RUBBER LATEX

Although the foregoing quantitative interpretation of the reaction of styrene and methyl methacrylate with rubber has been derived from experiments conducted in solution, the same state of affairs has been shown to exist in polymerizations conducted in rubber latex, irrespective of whether benzoyl peroxide or an activated hydroperoxide oxidation system was used. Persulfate initiation of methyl methacrylate gave substantially less graft polymer and, correspondingly, more free polymer.

On a technical scale, the preferred initiator for the preparation of graft polymers based on either styrene or methyl methacrylate was a polyamine-activated hydroperoxide⁷, since this gave high yields without the necessity of deammoniating or deaerating the latex.

TECHNOLOGY OF GRAFT POLYMERS

Hard vinyl polymers, such as styrene and methyl methacrylate, substantially reinforce rubber, whether present in simple admixture with rubber (designated mixed polymers) or as graft polymers in admixture with the concomitantly formed free polymer (the total composition is treated as graft polymer and is accordingly so designated in this paper). The graft polymers can be readily compounded and cured in conventional recipes to give light-colored articles of high tensile strength, and, in the case of rubber-methyl methacrylate, they show reduced hysteresis and outstanding resistance to flex cracking and fatigue. Stiffening at low elongations is greater with mixed polymers than with graft polymers, but is similar at higher elongations (more than 300 per cent); a given level of reinforcement in styrene graft polymers requires about 50 per cent more monomer than is the case with methyl methacrylate. Fuller details of the technical properties of these graft polymers will appear elsewhere⁸; softer vinyl polymers, as exemplified by the higher methacrylates, give less reinforcement as the size of the ester group is increased (Table 1).

Acrylates behave similarly to methacrylates in giving good yields of graft polymers in the presence of rubber, but the products are substantially different in that snappy insoluble materials are obtained if the polymerization is allowed to run to high monomer-conversion. These products undergo finite swelling in solvents and thus appear to be heavily cross-linked, although the cross-linkages are of an unusual type in that the material can be readily sheeted into a smooth velvety sheet on a cold mill. Although an infrared examination of cast films showed the unsaturation to be mainly intact, the acrylate graft polymers appear more resistant than raw rubber to thermal oxidation, and no useful vulcanizates can be obtained with either accelerated sulfur, peroxides, tetramethylthiuram disulfide, alkalies, or quinone dioxime recipes. Higher acrylic esters give similar materials. Consequently no technical information is available on acrylate graft polymers.

Progressive replacement of methyl methacrylate by ethyl acrylate in rubber-methyl methacrylate graft polymers reduces the modulus of the rubber-methyl

TABLE 1
TENSILE PROPERTIES OF RUBBER-METHACRYLATE GRAFT POLYMERS
(30 Parts methacrylate per 100 rubber)

Compounding: Polymer 100								
Zinc oxide							5.1	
Sulfur							2.5	
Stearic acid							1.0	
Santocure							0.6	
PBN							1.0	
Cure: 20 min. at 140° C								
	Tensile strength			M ₁₀₀		M ₁₀₀		Shore hard- ness
	Kg./ cm. ²	Lb./sq. in.	Eb. %	Kg./ cm. ²	Lb./ sq. in.	Kg./ cm. ²	Lb./sq. in.	
Methacrylate								
Methyl	280	3982	560	32	455	120	1706	75
Ethyl	240	3413	553	24	341	86	1223	63
Iso-butyl	225	3200	578	17	242	61	867	55
η -Butyl	190	2702	613	14	199	38	540	56
β -Ethoxy-ethyl	198	2816	735	9	128	18	256	53

methacrylate vulcanizate, without apparently introducing any advantageous feature (Table 2).

TABLE 2
TENSILE PROPERTIES OF ETHYL ACRYLATE-METHYL
METHACRYLATE GRAFT COPOLYMERS
(Compounding and Cure as Table 1)

Monomers polymerized per 100 rubber		Tensile strength			M ₁₀₀		M ₁₀₀		Shore hard- ness
MM	EA	Kg./cm. ²	Lb./sq. in.	Eb. %	Kg./cm. ²	Lb./sq. in.	Kg./cm. ²	Lb./sq. in.	
32	0	270	3839	550	38	540	128	1820	80
30	2	200	2844	420	36	512	125	1778	80
28	4	233	3313	483	26	370	112	1593	73
26	6	204	2901	448	30	427	111	1578	75
24	8	212	3015	455	25	356	111	1578	73

CROSS-LINKING AGENTS IN GRAFT POLYMERS

When a divinyl monomer is added to the styrene or methyl methacrylate used in the above systems, the graft polymer is modified by the cross-linking introduced between the polymeric side-chains and the free polymer, but substantial proportions of divinyl monomer can be added before the polymers become unprocessable. The modified polymers are generally harder, but the principal effect of the divinyl monomer is an enhanced tear resistance, which is otherwise poor in unmodified rubber-styrene or rubber-methyl methacrylate graft polymers.

POLYMERIZATION OF OTHER MONOMERS IN PRESENCE OF RUBBER

The polymerization of vinyl acetate is so severely retarded by rubber and polyisoprenes⁸ that it would be predicted that graft polymers derived from vinyl acetate cannot be prepared. Only the presence of high proportions of emulsifying stabilizers has led to any success in polymerizing vinyl acetate in rubber

latex, and under these conditions the monomer polymerized independently of the rubber to give a mixed product indistinguishable from that obtained by mixing rubber latex and a polyvinyl acetate emulsion. Possibly for similar reasons, vinyl chloride has not been successfully polymerized in the presence of rubber.

Although activated persulfate initiating systems are very efficient in bringing about the polymerization of vinylidene chloride and acrylonitrile in aqueous systems, they are singularly ineffective in promoting polymerizations of these monomers in rubber latex. The very active oxidation-reduction system comprising hydroperoxide/ferrous iron/dihydroxyacetone¹¹ proved much more effective, and high conversions of both monomers were obtained at 40° C in rubber latex stabilized with Lubrol-W or Perlancrol-C. No practical application has been found for the rubber-vinylidene chloride product, owing to its thermal instability, which was greater than that of the product obtained by simple admixture of rubber latex and polyvinylidene chloride latex. Its total

TABLE 3
PROPERTIES OF ACRYLONITRILE-MODIFIED RUBBER
AT OPTIMUM CURE¹⁰
Vulcanizing ingredients per 100 parts of rubber in polymer

Zinc oxide					5.0
Sulfur					3.0
Stearic acid					1.0
Santocure					0.7
PBN					1.0
Parts acrylonitrile per 100 rubber:	26	19		11.5	
Cure (min. at 140° C) (lb./in. ²)	30	40		40	
Tensile strength (kg./cm. ²)	82	(1166)	98	(1394)	69 (981)
Elongation at break (%)	223		295		210
M ₁₀₀ , kg./cm. ² (lb./in. ²)	51	(725)	32	(455)	34 (483)
M ₂₀₀ , kg./cm. ² (lb./in. ²)	75	(1067)	62	(882)	67 (953)
B. S. I. hardness	86		76		64
% Increase in length in:					
Benzene	36		44		48
Standard fuel	24		36		38
Oil	12		22		24

insolubility in a wide range of solvents and solvent pairs effectively prevented the application of separative procedures, as used for methyl methacrylate and styrene. Such gross insolubility was indicative of a graft polymer, but did not afford an unequivocal proof of structure, owing to the unknown effect of molecular entanglement and the known insolubilizing effect on rubber of the very active initiator used.

The same dihydroxyacetone initiating system has effected high conversions of acrylonitrile in rubber latex without having recourse to the high proportions of peroxidic initiators used by Compagnon and Le Bras². Again the product was too insoluble for structural analysis. Vulcanized acrylonitrile-modified rubber showed the anticipated resistance to solvents, but its elastic properties were very poor at the levels of acrylonitrile necessary to obtain effective resistance to solvents.

SUMMARY

Graft polymers result when vinyl monomers are polymerized in the presence of natural rubber, either in solution or as latex, and some of the polymeric chains become attached to the rubber molecules. The properties of the natural

rubber can be widely modified according to the nature and the amount of the grafted polymer. The polymer-modified natural rubber appears to be produced by direct growth of polymer chains on to rubber molecules rather than by a transfer reaction involving the rubber.

Graft polymers of styrene and methyl methacrylate with natural rubber can be compounded and cured to give light-colored articles of good tensile strength, and rubber-methyl methacrylate graft polymers have outstanding flex-cracking and fatigue resistance.

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GROWTH AND AGGLOMERATION OF PARTICLES IN LOW-TEMPERATURE GR-S TYPE OF LATEX*

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Previous developments in low-temperature polymerization of GR-S latexes at this laboratory have been published¹. This paper describes studies on the agglomeration of latex particles during and after polymerization.

AGGLOMERATION OF FINISHED LATEX

Medium- and low-solids latex recipes are characterized by faster and more uniform polymerization rates than are comparable high-solids recipes and, consequently, they give greater productivity in plant operation. Methods of agglomerating the resulting small particle-size latexes sufficiently to allow concentration to 50-60 per cent solids are therefore of interest, and several methods have been described². In addition, we have found that treatment of the latex with relatively large volumes of a solvent for the contained polymer causes smooth agglomeration.

TABLE I
AGGLOMERATION OF A MEDIUM SOLIDS LATEX WITH BENZENE

	Original	Agglomerated
Solids (per cent)	49.4	49.5
Viscosity (cps.)	780	35
Optical density* at 7000 A. U.	0.21	2.4
Average particle diameter, A. U.†	1000	3000
Relative number of particles per unit weight‡	100	4
Surface tension (dynes/cm.)	60.5	34.5
pH value	9.2	9.7

* The relation between optical density and particle size has been described by S. H. Maron in a private communication to the Federal Facilities Corp., Office of Synthetic Rubber.

† Unless otherwise stated, all particle sizes were estimated from optical density measurements at 7000 A. U. wave length.

‡ Calculated from average particle size.

Table I shows properties of a medium-solids GR-S latex (J-6083) before and after agglomeration with 80 per cent of its volume of benzene. The benzene was removed by steam distillation and the latex reconcentrated before testing. The polymerization recipes for this and other experimental latexes are in Table 2.

Several other water-insoluble organic solvents were also tried as agglomerating agents. In general, the hydrocarbons and their halogen derivatives were found to give smooth agglomeration, while more polar compounds such as diisobutylcarbinol and nonylphenol caused excessive coagulum. It appears that the effective agglomerating agents are those which act as solvents or swelling agents for the contained polymer. This point was confirmed by flocculating

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TABLE 2
 POLYMERIZATION RECIPES FOR EXPERIMENTAL LATEXES

	J-6083	J-6475 (X-753 Type)	J-6477 (X-758 Type)
Butadiene	50	86	70
Styrene	50	14	30
Water (total)	140	69	65
DIBH*	0.1	0.1	0.1
SFS†	0.1	0.15	0.05
FeSO ₄ ·7H ₂ O	0.003	0.002	0.003
EDTA‡	0.012	0.004	0.006
Potassium soap of disproportionated rosin acid	5.0	—	1.3
Potassium oleate	—	1.85**	1.7††
Dispersing agent§	—	0.74**	1.5
K ₂ SO ₄	—	—	1.2
Na ₃ PO ₄ ·12H ₂ O	—	0.26**	—
KCl	1.0	—	—
Sulfole¶	0.4	0.07	0.05
Shortstop, KDMDTC	0.2	0.2	0.2
Conversion (per cent)	85	37	60
Reaction time (hours)	37	14	57
Polymerization temp. (° C)	5	5	5

* Diisopropylbenzene hydroperoxide.

† Sodium formaldehyde sulfoxylate dihydrate.

‡ Ethylene diamine tetraacetic acid, tetrasodium salt.

§ Sodium salt of condensed naphthalenesulfonic acids.

¶ *Tert*-Dodecanethiol.

|| Potassium dimethyldithiocarbamate.

** Added in increments, 65% at start and 35% at 18% solids.

†† Added in increments, 59% at start and 41% at 25% solids.

samples of the polymer and immersing them in the various solvents. Solvents which gave smooth agglomeration dissolved the polymer or caused several hundred per cent swelling. Further confirmation of the relation between swelling and agglomeration was obtained by use of a cross-linking agent. A latex was prepared with 5 per cent divinylbenzene in the monomers to give insoluble polymer. Treatment of this material with benzene caused 30–60 per cent of the polymer to appear as coagulum. Normally the amount of coagulum does not exceed 1 per cent.

Differences in appearance of the latex during agglomeration are noticeable when solvents or nonsolvents for the polymer are used. Solvents cause a progressive thickening, or even gelation, usually followed by some thinning as ag-

 TABLE 3
 AGGLOMERATION OF A MEDIUM-SOLIDS LATEX WITH
 VARYING AMOUNTS OF BENZENE

Latex, ml. (50% solids)	100	100	100	100	100	100
Benzene (ml.)	—	12.5	25.0	37.5	50.0	75.0
% of polymer	—	25	50	75	100	150
Hydrocarbon*/H ₂ O ratio	1.0	1.2	1.5	1.8	2.0	2.5
Optical density	0.25	0.46	0.88	1.02	1.92	2.16
Average particle diameter (A. U.)	1000	1300	1850	1950	2650	2800
Relative number of particles per unit weight†	100	45	16	13	5	4

* Polymer plus benzene.

† Estimated from particle size.

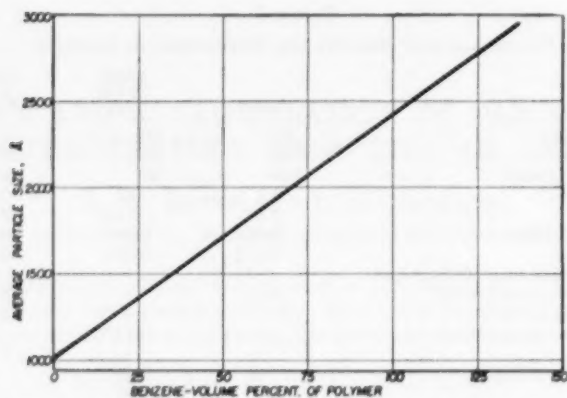


Fig. 1.—Effect of benzene on particle size of 50% GR-S type of latex.

glomeration occurs. When a nonsolvent is added, the latex remains fluid, and small particles of coagulum soon appear.

EFFECT OF VARYING AMOUNTS OF SOLVENT

In order to determine the amounts of solvent necessary for agglomeration, benzene was added in increments to a medium solids latex similar to J-6083 at 50 per cent solids. A small sample was removed after each increment, and the particle size measured. Table 3 shows that an amount of solvent equivalent

TABLE 4
AGGLOMERATION OF A MEDIUM SOLIDS LATEX WITH
VARYING AMOUNTS OF ISOPRENE

Isoprene, volume % of polymer	0	25	50	75	100	125	150
Hydrocarbon*/H ₂ O ratio	0.8	1.0	1.2	1.4	1.6	1.8	2.0
Optical density	0.35	0.37	0.39	0.49	0.63	0.88	1.15
Average particle diameter (A. U.)	1150	1200	1250	1400	1550	1800	2100
Relative number of particles/unit weight†	100	88	77	55	41	26	16

* Polymer plus isoprene.

† Approximated from particle size.

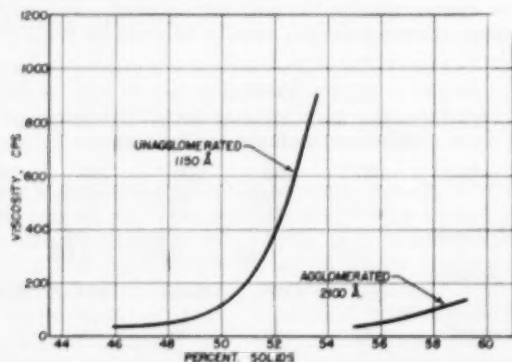


Fig. 2.—Viscosity of agglomerated and unagglomerated latexes.

TABLE 5

AGGLOMERATION WITH BENZENE AT VARYING
HYDROCARBON/WATER LEVELS

Latex (50% solids) (ml.)	200	200	200	200	Control*
Benzene (ml.)	100	100	100	100	—
Added H ₂ O (ml.)	—	14	33	60	—
Hydrocarbon/H ₂ O ratio†	2/1	1.75/1	1.50/1	1.25/1	—
Optical density	1.13	0.64	0.42	0.31	0.25
Average particle size, (A. U.)	2000	1600	1300	1100	1000
Surface tension (dynes/cm.)	46	57	62	—	64

* Untreated base latex.

† Polymer plus benzene.

‡ Volume ratios.

to 50-75 per cent of the volume of the polymer was necessary to increase the particle size to the range necessary for high solids latex. In Figure 1 the particle size is shown as a function of the amount of benzene added.

Since practical application of this method of agglomeration in a synthetic-rubber plant would probably involve the use of butadiene as the solvent, it

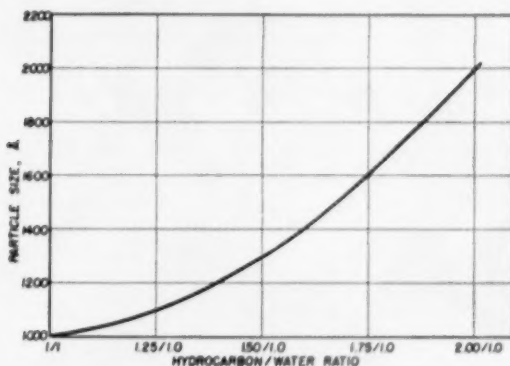


FIG. 3.—Effect of hydrocarbon/water ratio on agglomeration of medium-solids latex.

appeared desirable to carry out an agglomeration with it or a related compound. Isoprene was substituted for butadiene because of its comparative ease of handling. Table 4 shows the results of agglomerating a medium-solids latex at 45 per cent solids with increments of isoprene.

A comparison of the data of Tables 3 and 4 indicates that benzene is a somewhat more efficient agglomerating agent than isoprene on an equal volume basis.

TABLE 6

AGGLOMERATION WITH VARYING AMOUNTS OF BENZENE AT A CONSTANT
HYDROCARBON/WATER RATIO

Latex (50% solids) (ml.)	200	200	200
H ₂ O (ml.)	—	12.5	25
† Benzene (ml.)	100	125	150
‡ Optical density	1.42	1.85	1.98
Average particle diameter (A. U.)	2300	2600	2700

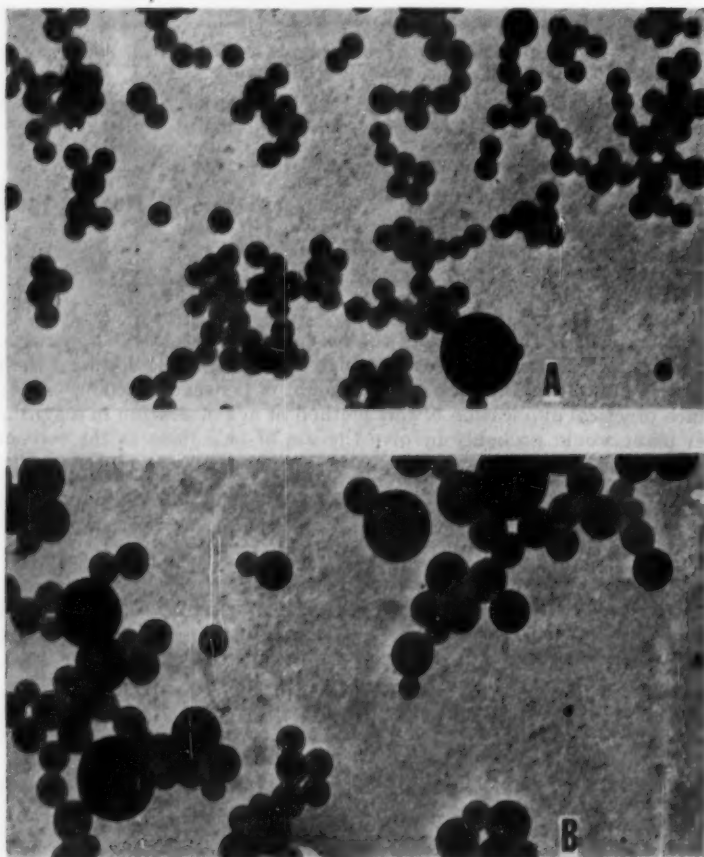


FIG. 4.—Electron photomicrographs showing particle growth during solvent agglomeration of medium-solids latex (magnification, 48,000 times). A—0% benzene; B—50% benzene; C—75% and D—150% benzene.

Some of this difference, however, is due to the difference in solids content of the latexes, a variable to be discussed in the following section.

The relative numbers of particles shown in Tables 3 and 4 are only an approximation, but were calculated to emphasize the very large decrease in particle number which is brought about by agglomeration. Figure 2 shows a comparison of viscosity characteristics of agglomerated and unagglomerated samples (original and final latexes of Table 4). It is apparent that the agglomerated sample has good viscosity characteristics in the 60 per cent solids range.

EFFECT OF HYDROCARBON/WATER RATIO

The first work was carried out without much regard for the hydrocarbon/water ratio. If the latex became jelled, additional water was added to aid in agitation. Variable results led to a study of the effect of this ratio. Table 5

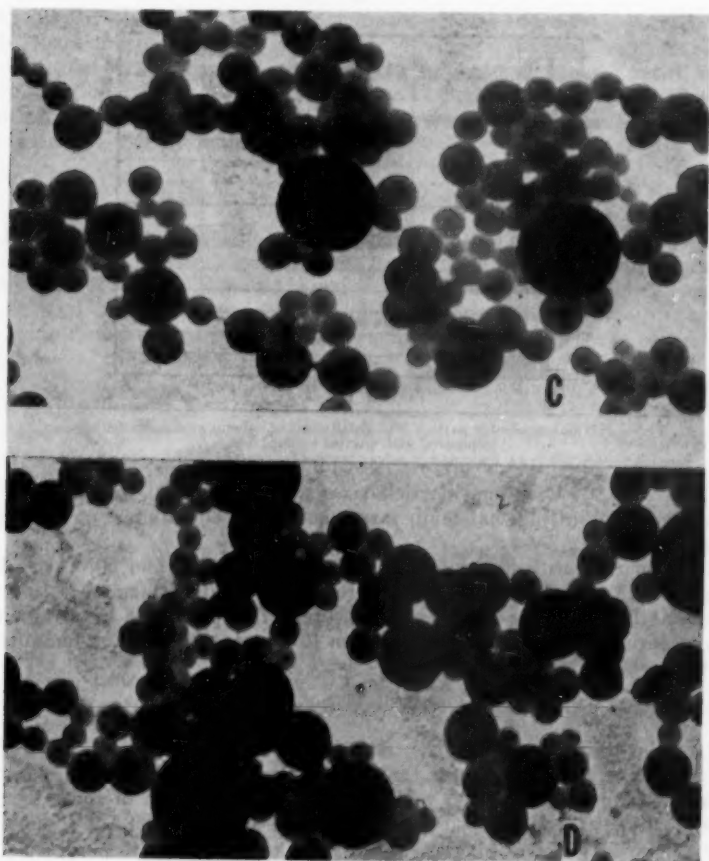


FIG. 4—Continued

and Figure 3 show the results of agglomerating a medium water latex with a constant volume of latex and benzene, but with the addition of varying amounts of water.

It is apparent that the hydrocarbon/water ratio exerts a large effect on the amount of agglomeration. To confirm these data, another series of runs was made in which the latex was diluted with water, but the hydrocarbon/water ratio was maintained constant at 2/1 ratio by increasing the amount of benzene added. Table 6 shows that, under these conditions, the amount of agglomeration increased somewhat, presumably owing to the higher hydrocarbon/soap ratio.

EFFECT OF TEMPERATURE

In order to determine the effect of temperature on the extent of agglomeration, experiments were carried out in which a medium solids latex was agglomerated at 50 per cent solids with toluene (100 volume per cent of latex solids)

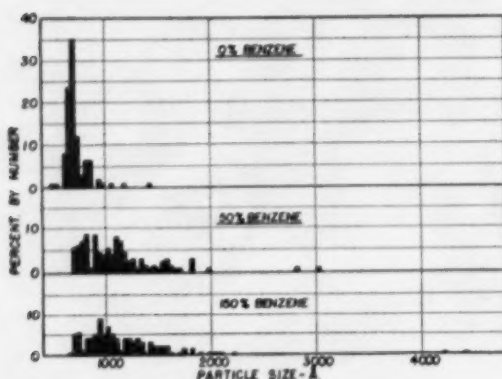


FIG. 5.—Number average particle-size distribution of solvent agglomerated latexes compared with control with solvent.

at 2, 50, and 80° C. Final particle sizes were 2600, 2700, and 2750 Å. U., respectively, indicating that temperature has only a slight effect on the extent of agglomeration.

In other runs with benzene as the agglomerant at 26 and 50° C in which samples were taken at various time intervals, the rate of agglomeration was somewhat faster at the higher temperature. The process is rapid at either temperature, being essentially complete in 40 minutes at 25° and 20 minutes at 50° C.

EFFECT OF SOAP AND DISPERSING AGENT

In order to determine whether additional soap would prevent solvent agglomeration, a 1000-Angstrom latex³ containing five parts of soap per hundred of polymer was agglomerated with benzene, after addition of three parts of disproportionated rosin soap. The final particle size was 2200 Å. U., compared

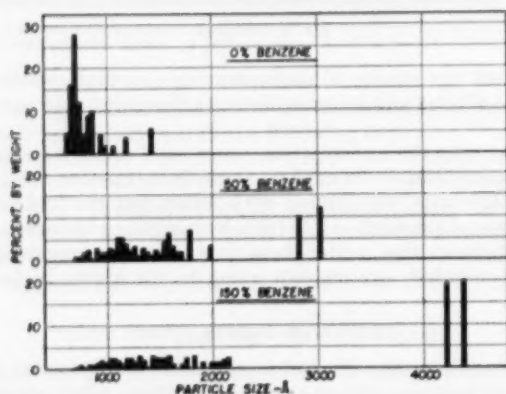


FIG. 6.—Weight average particle-size distribution of solvent agglomerated latexes compared with control.

to 2500 A. U. for a control latex agglomerated with no added soap. Apparently additional emulsifier has only a moderate effect on this type of agglomeration.

Addition of a condensed naphthalene sulfonate dispersing agent before agglomeration appeared to have little or no effect on agglomeration, but decreased viscosity both during and after treatment. Table 7 shows agglomeration with and without added dispersing agent.

CHANGES IN PARTICLE-SIZE DISTRIBUTION

In order to determine the effect of agglomeration on particle-size distribution, electron photomicrographs were taken of the agglomerated samples described in Table 3. Figure 4 shows sections from some of these photomicrographs, and in Figures 5 and 6 the number and weight distribution for three of the samples are shown. It should be emphasized that, because of the very large mass of the largest particles and their infrequent occurrence compared to the small ones, it is impossible to obtain a smooth distribution curve from these photographs, except by counting a prohibitively large number of particles. It is also very difficult to get a good value for the weight per cent represented by the large particles, although the relative numbers can be determined quite accurately.

TABLE 7
EFFECT OF DISPERSING AGENT ON SOLVENT AGGLOMERATION

Latex (50% solids) (ml.)	200	200	Control*
Benzene (ml.)	100	100	—
Dispersing agent†	—	2.0	—
Optical density	2.17	2.10	0.25
Particle size (A. U.)	2850	2800	1000
Concentrated solids (%)	62.7	67.5	51.0
Viscosity (cps.) (Brookfield)	340	1200	1680

* Untreated base latex.

† Sodium salt of condensed naphthalenesulfonic acids.

The photomicrographs, however, do show that in the original latex the majority of particles (about 80 per cent) were in the range of 600 to 800 A. U. As agglomeration proceeded, the particles appear to have merged randomly with a consequent wide distribution, in which no particular size predominated. Even in the most extensively agglomerated sample, there were still appreciable numbers of 700 to 800 Angstrom particles, although their contribution to the total weight had become negligible. The very large relative amount of weight represented by two particles in each of the agglomerated samples (Figure 6) emphasizes the difficulties referred to earlier.

AGGLOMERATION DURING POLYMERIZATION OF HIGH SOLIDS LATEX

PARTICLE GROWTH AS A FUNCTION OF CONVERSION

A consideration of the conditions during agglomeration of these medium-solids latexes shows that they are quite similar to those existing at intermediate conversions of high-solids latex recipes. For example, a system containing 100 parts of latex at 50 per cent solids agglomerated with 50 per cent of its weight of benzene (50 parts water, 50 parts polymer, 50 parts benzene) is very similar to a high-solids latex at 50 per cent conversion (50 parts water, 50 parts polymer,

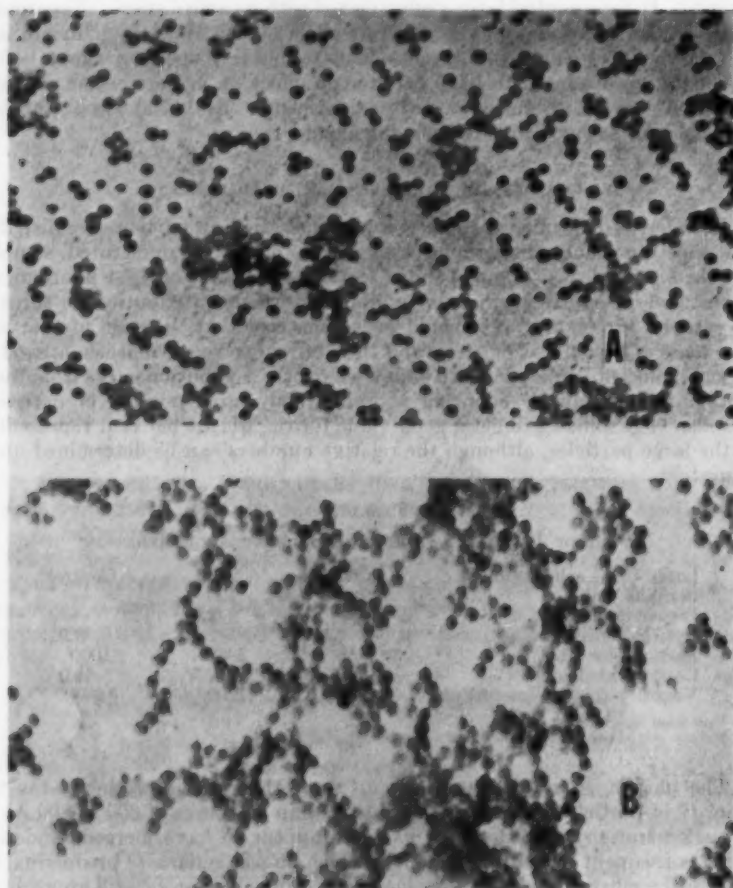


FIG. 7.—Particle growth of X-753, high solids, GR-S type of latex during polymerization (magnification, 48,000 times). A—12.5% conversion; B—26.5% conversion; C—37% conversion; D—37% conversion—70 hours' aging.

50 parts monomers). It therefore appeared that extensive solvent agglomeration must go on during polymerization. To check this assumption a 20-gallon pilot-plant batch of X-753 type of latex (J-6475) was prepared and sampled at various conversions. Since, at the time this work was done, it appeared that the agglomeration might be occurring over a relatively long period

TABLE 8
PARTICLE GROWTH IN J-6475 (X-753 TYPE) LATEX

Hours of polymerization	5.25	10.25	14.0	14.0	14.0	14.0	14.0
After shortstop	—	—	—	5	15	25	70
Conversion (%)	12.5	26.5	37.0	37.0	37.0	37.0	37.0
Optical density	0.03	0.032	0.51	0.57	0.63	0.71	0.84
Average particle size (A. U.)	400	400	1400	1480	1550	1650	1800
Relative number of particles (470)	—	1000	33	26	24	20	15
Solids at 1000 cps. viscosity (%)	—	—	54.8	—	—	55.8	57.6

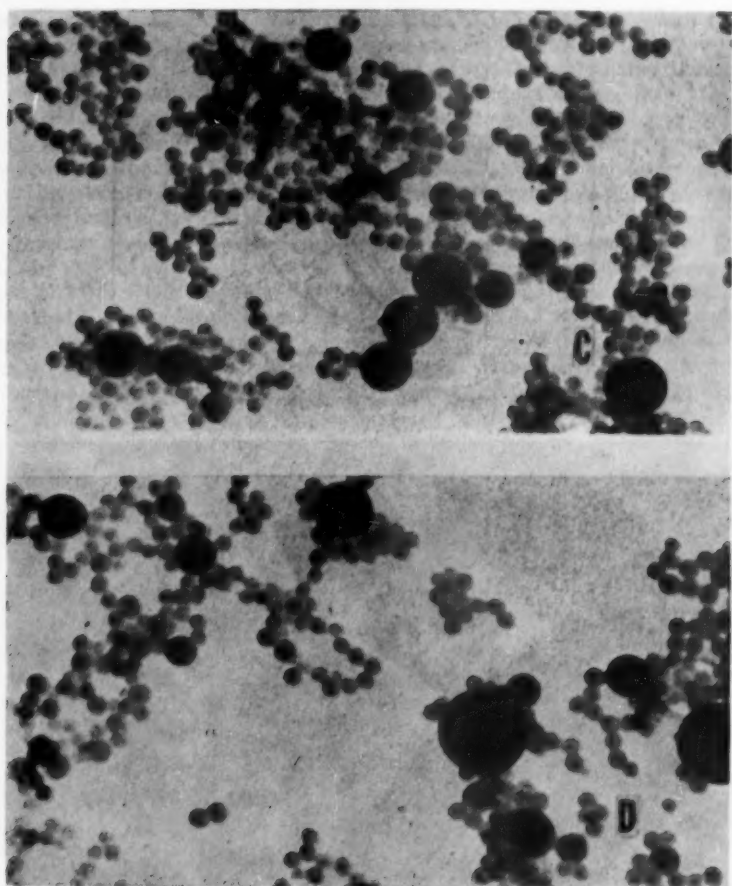


FIG. 5—Continued

of time, the batch was not completed, but short-stopped at 37 per cent conversion and held in the reactor for an additional 70 hours. Data are collected in Table 8. The polymerization recipe is shown in Table 2.

It is apparent that in the initial stages of polymerization this latex contained far too many particles for a high-solids latex. Calculation shows that a latex with an average particle size of 400 A. U. at 26 per cent conversion, which increases in particle size only by uniform growth of particles already present, will have an average particle size of only 530 A. U. at 60 per cent conversion ($400 \times \sqrt[3]{60/26}$). The abrupt increase of particle size between 26 and 37 per cent conversion must be attributed to some other factor, apparently solvent agglomeration caused by unreacted monomers dissolving in the latex particles. This agglomeration also can explain the typical decrease of polymerization rate normally found in high-solids latex recipes between 20 and 30 per cent conversion. The relative number of particles given in Table 8 shows that only

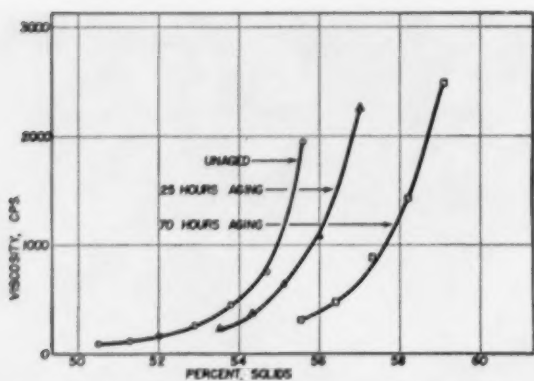


FIG. 8.—Effect of aging in reactor on the viscosity of X-753 latex.

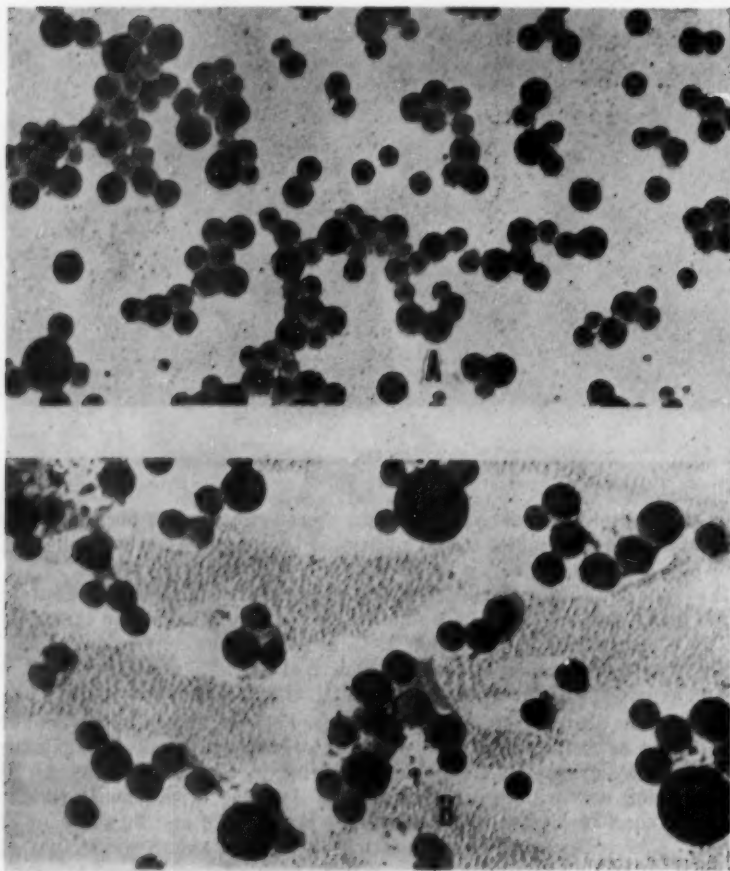


FIG. 9.—Particle growth of X-758, high solids, GR-8 type of latex during polymerization (magnification, 48,000 times). A—12% conversion; B—20% conversion; C—28% conversion; D—60% conversion.

about 3 per cent of the initial number was left after agglomeration. This figure is an approximation, but it obviously is small enough to have a severe effect on polymerization rate if an approximation of the theory⁴ that polymerization rate per particle is constant in emulsion polymerization holds in these recipes.

Electron photomicrographs of the first three and the final samples of Table 8 are reproduced in Figure 7. The photomicrographs correlate well with the data discussed above. The first two samples (12.5 and 26.5 per cent conversion) show a small particle size, nearly monodisperse latex; while the 37 per cent conversion sample has many large particles, although the minimum particle size increases about as would be expected from the per cent conversion. (A measured ratio of average diameters of the smallest particles in the three micrographs of 1.0/2.1/3.3 was obtained compared to a calculated ratio of 1.0/2.2/3.0.) Had polymerization been allowed to continue, of course, the smaller particles would have grown faster than would be calculated from the conversion increase, owing to the bulk of relatively inactive large particles. The final micrograph, taken after 70 hours' aging, shows no change of size of the basic

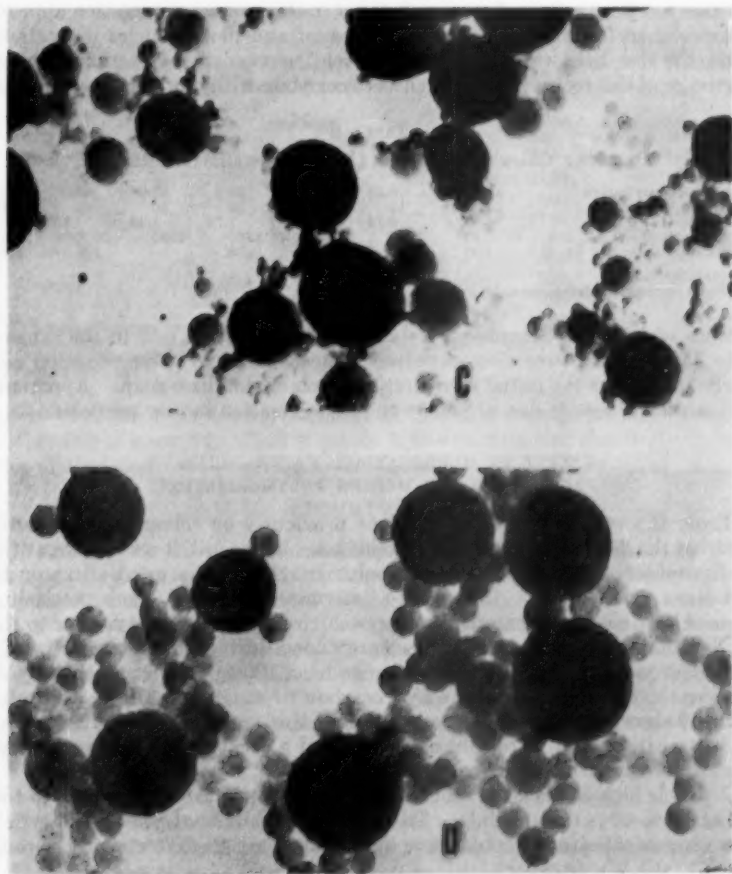


FIG. 9—Continued

particles, and, as would be expected from the random scattering of large particles, appears visually like the third sample, taken before aging, although the average particle size has increased considerably.

Viscosity vs. solids curves (Figure 8) show a slow progressive improvement on aging in the reactor, correlating with the increased particle size found by turbidity measurement. The magnitude of this slow growth is small, however, compared to the rapid initial agglomeration.

Another pilot-plant batch, J-6477 (GR-S 2105 type) was sampled and studied at various conversions up to 60 per cent. Data are collected in Table 9. The polymerization recipe is shown in Table 2.

In this latex, agglomeration started much earlier and was more extensive than was the case with J-6475. Another unexpected result was the decrease of average particle size between 36 and 45 per cent conversion. An examination of the electron photomicrographs (Figure 9) shows that an extensive group of new particles was formed as early as 28 per cent conversion and was apparently responsible for decreasing the average particle size.

The formation of new particles in X-758 (GR-S 2105) latex after stabilizer addition has been reported previously⁴, but in this case agglomeration appeared to proceed so far that free soap was released and new particles were started before the stabilizer was added at 36 per cent conversion. Reaction rate characteristics of this recipe are also such as to correlate with new particle formation.

TABLE 9
PARTICLE GROWTH IN J-6477 (X-758 TYPE) LATEX RECIPE

Hours of polymerization	3.25	6.25	16.0	29.0	35.0*	44.0	57.0
Conversion (%)	3	12	20	28	36	45	60
Optical density	0.14	0.16	0.61	1.75	1.93	1.35	1.23
Average particle size (A. U.)	720	770	1500	2550	2650	2250	2150
Minimum particle size† (A. U.)	300	400	700	400	—	700	900

* Stabilizer added.

† From electron photomicrographs.

Batches which have become very slow in polymerization rate in the range of 25 to 35 per cent conversion can often be accelerated to polymerization rates nearly as rapid as the initial rate after addition of stabilizer soap. Apparently the increase of rate is due primarily to polymerization in new particles.

EFFECT OF HYDROCARBON/WATER RATIO ON AGGLOMERATION DURING POLYMERIZATION

From the work which has been done previously on solvent agglomeration and from the development of higher solids latex in general, it was apparent that the hydrocarbon/water ratio during polymerization has a great effect on the final latex particle size. In order to determine this effect more precisely, a series of bottle-scale polymerizations was carried out in a recipe similar to that for X-753 except that no stabilizers were added during polymerization. The amount of monomer was reduced stepwise from 100 to 6.25 parts, thereby decreasing the volume ratio of the hydrocarbon to water phase from 2.9 to 0.2. Table 10 shows results. It is apparent that this variation in volume ratio of the hydrocarbon and water phases has caused a great change in average particle size of the resulting latexes.

A usable high-solids latex should have a viscosity in the range of 500 to 1500 cps. at 58 to 60 per cent solids. To meet this requirement, the X-753 type of latex used in this study should have an average particle diameter in the range

of 1800 A. U. or above. Figure 8 and Table 8 show that J-6475 (X-753 type) latex reached a viscosity of 1500 cps. at about 58 per cent solids. This batch, however, differs from regular X-753 in that it was shortstopped at 37 per cent conversion, and the final stabilizer was not used. The addition of the electrolyte and dispersing agent contained in this final stabilizer would have reduced the viscosity to the desired range at 60 per cent solids or higher. A study of the data in Table 10 shows that the latex polymerization recipe must have less than 75 parts of water per 100 parts of monomers in order to give the desired particle size for a fluid 60 per cent or higher solids latex.

The exact particle size necessary for fluidity at 60 per cent solids varies somewhat with different formulations, as does the hydrocarbon/water ratio necessary to obtain it. For example, the X-758 recipe (Table 2), because of its high level of electrolyte (which helps cause agglomeration), gives a larger particle size at about the same hydrocarbon/water ratio than does X-753 (compare Tables 8 and 9). In addition, higher electrolyte and dispersing agent

TABLE 10
EFFECT OF MONOMER/H₂O RATIO ON PARTICLE SIZE

Polymerization recipe: B/S variable (70/30 ratio), DIBHP* 0.1, SFS† 0.1, FeSO₄ · 7H₂O 0.002, EDTA‡ 0.004, K oleate 2.0, Dispersing agent 1.0, Na₂SO₄ 0.5, H₂O 50.

Monomers charged	Hydrocarbon/H ₂ O Ratio§	H ₂ O/100 g. of monomers	Optical density	Particle size (A. U.)	Relative no. of particles per unit weight
100	2.0	50	1.16	2100	4
67	2.0	75	0.66	1600	7
50	1.5	100	0.35	1150	12
33	1.0	150	0.10	700	32
25	0.7	200	0.036	500	55
12.5	0.4	400	0.012	320	106
6.2	0.2	800	0.008	250	100

* Diisopropylbenzene hydroperoxide.

† Sodium formaldehyde sulfoxylate dihydrate.

‡ Ethylene diamine tetraacetic acid, tetrasodium salt.

§ Volume ratio at 0% conversion.

content of X-758 gives a lower viscosity at the same average particle diameter. Another factor known to affect viscosity is the particle size distribution⁶, with wider distribution usually giving lower viscosity.

CONCLUSIONS

It has been shown that it is possible to prepare high-solids latex by polymerizing to an intermediate solids content and particle size, followed by solvent agglomeration and concentration. It has also been shown that a somewhat similar agglomeration normally takes place at intermediate conversions in conventional high-solids latex recipes. The slow rates of polymerization in the latter recipes after agglomeration are primarily due to the greatly reduced number of particles present. The ratio of hydrocarbon to water is very important in determining the extent of agglomeration both during and after polymerization.

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- ³ To convert Angstrom units to microns, multiply by 0.0001.
- ⁴ Smith and Ewart, *J. Chem. Phys.* **16**, 592 (1948); Smith, *J. Am. Chem. Soc.* **70**, 3695 (1948).
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STUDY OF THE KINETICS OF POLYMERIZATION OF ISOPRENE IN AQUEOUS SOLUTIONS OF EMULSIFIERS AND IN EMULSIONS *

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It has been established earlier¹ that polymerization in aqueous solutions of emulsifiers takes place in the water or in the micellae of the emulsifier, depending on the solubility of the monomer and the initiator. The question of the topochemical properties of polymerization in emulsions has not yet been definitively explained. In a number of studies², the hypothesis was advanced that the process of emulsion polymerization takes place in the micellae of the emulsifier, according to the degree of conversion of the micellae into polymer-monomer particles, with the monomer dissolved in the polymer.

In order to explain further the mechanism of emulsion polymerization, the kinetics of polymerization of isoprene in water, in solutions of emulsifier and *N*-cetylpyridinium bromide, and in emulsions in the presence of a water-soluble initiator (hydrogen peroxide) were studied. The dilatometric method was chosen for the kinetic measurements of solutions of emulsifier not saturated with isoprene, and for emulsions. Experiments with solutions of emulsifier saturated with monomer were made during continuous saturation of the emulsifier-initiator solution with isoprene in the gaseous phase. All the experiments were made at 50° C in the absence of oxygen.

Polymerization of isoprene is not observed if the reaction takes place in a water solution of initiator without emulsifier. The addition of an emulsifier to such a system greatly accelerates polymerization, for the rate of the reaction depends to a large degree on the concentration of emulsifier and the micellar concentration of monomer. Thus, in the case of polymerization in *N*-cetylpyridinium bromide at concentrations of 11.1 ÷ 71.3 g. per l., saturated with isoprene, that is, at constant micellar concentration of isoprene, the rate of the reaction is proportional to the concentration of emulsifier. An increase of the micellar concentration of isoprene causes an increase of the rate of polymerization (see Figure 1). An increase of the concentration of emulsifier in solution from 9.87 to 64.3 g. per l. with the same total quantity of isoprene (which corresponds to a decrease of the micellar concentration of isoprene from 0.338 to 0.0635 g. per g.) decreases the rate of polymerization from 2.38 to 1.22 g. per l. per hr.

From the relations obtained, it follows that, during polymerization in emulsifier solutions, in the zone of colloidal solution of the monomer the micellae of the emulsifier are the location of the elementary polymerization reactions.

In the case of polymerization in emulsions, the rate of the reaction in the initial period during a change of emulsifier concentration from 9.85 to 63.4 g. per l. is proportional to its concentration in the water phase. This indicates

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Doklady Akademii Nauk SSSR*, Vol. 97, No. 1, pages 111-114 (1954).

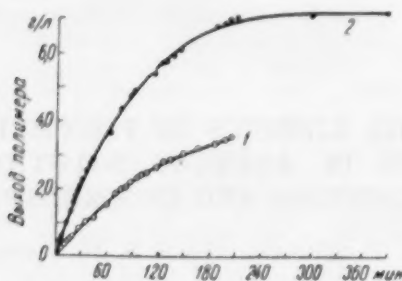


Fig. 1.—Kinetics of polymerization of isoprene in *N*-cetylpyridinium bromide (CPB) solutions not saturated with monomer. CPB concentration 28.9 g. per l. H_2O_2 concentration 4.6 g. per l. C_5H_8 concentration: (1) 0.129 g. per l. of CPB; (2) 0.289 g. per l. of CPB. The ordinate indicates the yield of polymer in grams per liter; the abscissa the time in minutes.

that here, too, the reaction takes place chiefly in the micellae of the emulsifier in the early stages. Globules of an emulsion of the monomer in the case of water-soluble initiators can not serve as nuclei of the reaction, because of the very small concentration of peroxide in them. As the reaction proceeds, the micellae of the emulsifier with the monomer dissolved in them are converted into polymeric particles surrounded by an adsorption layer of emulsifier.

Experiments carried out in solutions of emulsifier continuously saturated with monomer (see Figure 2) show that, after a short changing period, the rate of polymerization remains constant with time and does not depend on the accumulation of polymer and dissolved monomer in the latex, but on the distribution of emulsifier between the micellae and the adsorption layers on the polymeric particles. This distribution changes during polymerization. It was established by special experiments that the amount of dissolved isoprene x_r depends linearly on the concentration of polymer x_p in the latex and comprises about 55 per cent of the weight of the polymer:

$$x_r = x_{kr} + \alpha \cdot x_p$$

where x_{kr} is the solubility of isoprene in the colloid, at a given concentration of emulsifier in latex; α is the solubility of isoprene in the polymer (equal to 0.543).

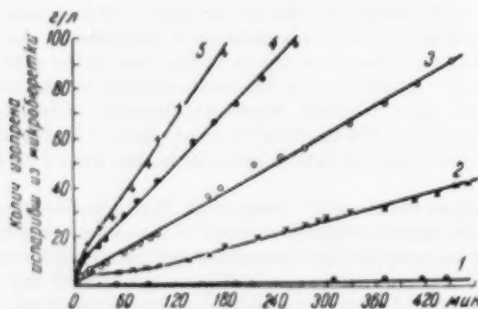


Fig. 2.—Kinetics of polymerization in *N*-cetylpyridinium bromide (CPB) solutions saturated with isoprene. H_2O_2 concentration 6.7 g. per l. CPB concentration: 1. 0.0 g. per l. 2. 9.9 g. per l. 3. 28.9 g. per l. 4. 46.9 g. per l. 5. 64.2 g. per l. The ordinate indicates the quantity of isoprene evaporated from the microburette, in grams per liter; the abscissa, the time in minutes.

Polymerization in emulsions is also characterized by a constant rate with time, up to about 50 per cent conversion (see Figure 3).

The hypothesis that, after conversion of the micellae of emulsifier, with the monomer dissolved in them, into polymeric particles, the reaction proceeds in the polymeric particles² is not in accordance with the fact that the rate of the reaction observed in the experiment is constant. In fact, if polymerization took place in the polymeric particles, then the increase of size of the particles at the expense of accumulation of polymer and swelling of the polymer in the monomer would inevitably lead to an increase of the rate of the reaction with time. Furthermore, the increase of the amount of monomer dissolved in the polymeric particles (in the experiments illustrated in Figure 2) also must increase the rate.

Various possible polymerization mechanisms, differing in the location of the elementary steps in the process, were studied. The relations obtained for the rate of polymerization, derived on the assumption that the reaction takes place in the monomer-polymer particles, contradict the experimental data, as one would expect. The rate can be constant with time only if we assume that all

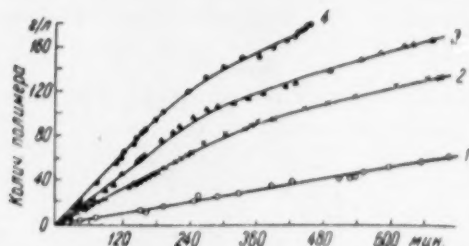


Fig. 3.—Polymerization of isoprene in emulsions. H_2O_2 concentration 6.7 g. per l. Ratio of hydrocarbon-water phases 1:3.7. CFB concentration: (1) 9.85 g. per l. (2) 28.6 g. per l. (3) 46.3 g. per l. (4) 63.4 g. per l. The ordinate indicates the quantity of polymer in grams per liter; the abscissa the time in minutes.

the elementary polymerization reactions (initiation, growth, and rupture of the chains) take place on the surface of the polymer particles, while the latter remains constant throughout the reaction.

Analysis of electron-microscope photographs obtained during the present study of latexes of various degrees of polymerization shows that fusion of the polymer particles takes place during polymerization. This is confirmed by the data of other authors³, and is explained by the fact that a given quantity of emulsifier covers, with the adsorption layer which protects the particles from fusion, only a definite surface area. Hence an increase of the total surface area of the polymer particles during polymerization beyond a certain limit must lead to coalescence.

Thus a constant quantity of emulsifier in the system means a constant total surface area of the polymer particles during polymerization. The constant total surface area of the particle, as well as the constant rate of the reaction with time for experiments in saturated solutions and emulsions leads to the conclusion that polymerization takes place in the adsorption layer of the emulsifier on this surface. Polymerization in the adsorption layer of the emulsifier is caused by the fact that, in this layer, the largest quantities of both monomer and initiator are present at the same time.

This theory is also confirmed by the experimentally observed relation between the rate of polymerization and the concentration of peroxide in aqueous solution; this can be represented by the following equation:

$$w^2 = \frac{\beta \cdot k'' \cdot C_{H_2O_2}}{k''' + k'' \cdot C_{H_2O_2}} \quad (1)$$

where $C_{H_2O_2}$ is the concentration of initiator in water solution.

This equation, which resembles that of the isotherm of adsorption, indicates the distribution of initiator between the water solution and the surface layers of the micellae and polymeric particles.

The maximum value of the rate of polymerization, which can be established by starting with a small concentration of hydrogen peroxide in aqueous solution, corresponds to the saturation of the surface layer by the initiator.

Thus, the polymerization process at any stage takes place in the emulsifier layer, at first in the soapy micellae, and then, as the polymer particles grow, in the adsorption layer on the surface of the particles. The part of the process which takes place in the adsorption layers of emulsifier on the surface of the drops of emulsion is quite small. As the polymer particles grow, the adsorption

TABLE I
VALUES OF k IN 0.5 LITER PER GRAM PER 0.5 HOUR⁻¹

CPB concentration (g. per l.)	In saturated solutions	In saturated solutions	In emulsions
9.9	1.77	2.07	4.62
28.9	1.74	2.18	4.25
47.0	2.13	2.19	4.40
64.3	1.82	2.18	4.42
Average	1.87	2.15	4.42

layer of emulsifier is displaced in the direction of the water phase, while remaining on the surface of the particles. Polymerization does not take place in the monomer dissolved in the polymer particles, owing to the exceptionally low concentration of initiator in the polymeric particles.

An equation was derived, on the basis of this theory, for the rate of polymerization in aqueous solutions of emulsifier and in emulsions, according to the experimental data:

$$w = \frac{1.41 k_1^{0.5} k_r \sqrt{\frac{\gamma \cdot k'' \cdot C_{H_2O_2}}{k''' + k'' \cdot C_{H_2O_2}}} \cdot a^1}{k_{ab}^{0.5} \cdot v_M^{0.5}} \quad (2)$$

where w is the total rate of the reaction, k_1 is the constant of the rate of reaction of hydrogen peroxide with the monomer; k_r , k_{ab} are the constants of rate of growth and rupture, respectively; γ is the concentration of hydrogen peroxide in the surface layers of emulsifier during saturation, k'' and k''' are constants expressing the probability of transfer of the molecules of hydrogen peroxide from the water solution into the surface layers of the micellae particles and the opposite process, respectively. Their values can be determined from Equation (1); $C_{H_2O_2}$ is the concentration of hydrogen peroxide in aqueous solution; a is the amount of monomer dissolved in the emulsifier; and v_M is the volume of the emulsifier with the monomer dissolved in it.

At equal concentrations of hydrogen peroxide in water solution, the value of

$$\frac{1.41k_1^{0.5} \cdot k_r \sqrt{\frac{\gamma \cdot k'' \cdot C_{H_2O_2}}{k''' + k'' \cdot C_{H_2O_2}}}}{k_{ab}^{0.5}} = k = \text{const.}$$

The constants k , calculated according to Equation (2) from experiments performed under varying conditions, remain satisfactorily constant (see Table 1).

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THE RELATION BETWEEN THE OXIDATION AND CHANGE OF STRUCTURE OF A BUTADIENE-STYRENE RUBBER *

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Until the present no quantitative relation had been established between speed and length of time of oxidation of rubber, on one hand, and the character and degree of the corresponding structural changes, on the other. The present work is an attempt to fill this gap.

The specimen under investigation was a heat-vulcanizate of butadiene-styrene rubber¹ containing 1 per cent of phenyl-2-naphthylamine. Oxidation took place in air at 100° and 120° C. The kinetics of the consumption of phenyl-2-naphthylamine is presented in Figure 1. The modulus of elasticity, E_m , was chosen as the index of structure.

Figures 2 and 3 present the kinetics of the change in the quantity E_m in the process of oxidation of the vulcanizate.

In previous work² we established that the speed of oxidation of nonpolar rubbers in the presence of phenyl-2-naphthylamine could be determined from this antioxidant's speed of combination, W_i .

Assuming that the phenyl-2-naphthylamine reacts with the active centers in the exact stoichiometric proportions, we showed that W_i equaled the speed of initiation of oxidized chains. In the presence of phenyl-2-naphthylamine only fairly short primary chains are possible, whose presence determines the change in structure of the rubber during oxidation.

The equation for speed of formation and rupture of the initial active centers (n_0) with which phenyl-2-naphthylamine reacts determines the steadiness of the reaction and, consequently, the constancy of W_i in time.

From the conditions of steadiness we have:

$$+ \frac{d[n_0]}{dt} = - \frac{d[b]}{dt} = W_i = K_i[\Pi][O_2] = K_n[n_0][b] \quad (1)$$

where K_i and K_n are constants of speed; $[\Pi]$ is the concentration of double bonds in the rubber, which is practically unchanged during the whole time in which phenyl-2-naphthylamine reacts; $[O_2]$ is the concentration of oxygen, which is constant under the conditions of the test³; $[b]$ is the concentration of phenyl-2-naphthylamine and $[n_0]$ is the concentration of active centers.

From (1) it follows (considering that $W_i = b_0/t_{max}$) that:

$$[n_0] = \frac{W_i}{K_n[b]} = \frac{W_i}{K_n(b_0 - W_i t)} = \frac{1}{K_n \Delta t} \quad (2)$$

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Doklady Akademii Nauk S.S.S.R.*, Vol. 86, No. 6, pages 1147-1150 (1952).

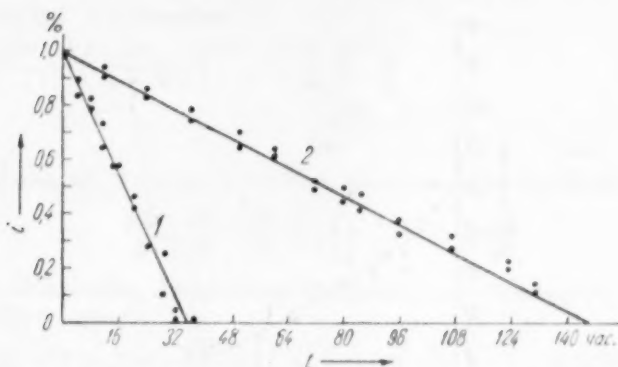


Fig. 1.—Kinetics of consumption of phenyl-2-naphthylamine in the process of oxidation of a vulcanizate. 1. Oxidation at 120° C. 2. Oxidation at 100° C. The abscissa represents the time of oxidation in hours; the ordinate the free phenyl-2-naphthylamine content i .

where t_{\max} is the length of time required for complete reaction of phenyl-2-naphthylamine; b_0 is the original concentration of this antioxidant in rubber; t is the length of time of oxidation, and $\Delta t = t_{\max} - t$.

According to present-day ideas, in rubber oxidation the initial active center π_0 is an active (radical) form of peroxide, the spontaneous decomposition of which (probably extensive) is connected with the rupture of the adjacent C=C

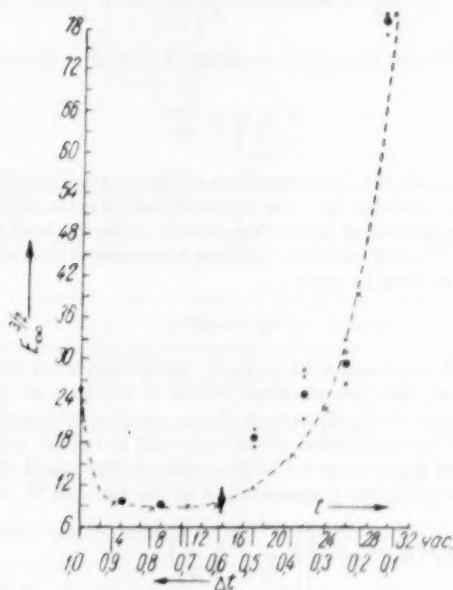


Fig. 2.—Change in the quantity E_{π} in the process of oxidation of a vulcanizate at 120° C. The broken line is the theoretical curve. The upper scale of the abscissa represents the time of oxidation in hours.

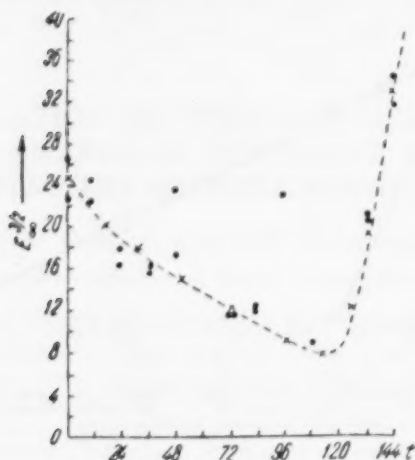


FIG. 3.—Change in the quantity $E_{\omega}^{\frac{1}{2}}$ in the process of oxidation of a vulcanizate at 100° C. The broken line is the theoretical curve. The abscissa represents the time of oxidation t in hours.

bond; i.e., with the elementary act of destruction. Therefore the rapidity of destruction dZ/dt should be proportional to the quantity $[n_0]$:

$$\frac{dZ}{dt} = K_3[n_0] = \frac{K_3}{K_n} \frac{W_i}{[b]} = K \frac{1}{\Delta t} \quad (3)$$

Integrating with the apparent condition: $t = 0, Z = 0$, we get

$$Z = K \ln \frac{t_{\max}}{\Delta t} \quad (4)$$

On the other hand, the decomposition of the original center n_0 leads to the formation¹ of free radicals R . An approximate thermochemical calculation shows that decomposition of one active center n_0 cannot lead to the formation of two radicals. It must be noted that on a statistical average m radicals are formed, where m is close to unity:



The radicals R can react with oxygen, being converted into inactive compounds⁴; recombine with one another (which in the case of rubber is improbable); and react with the hydrocarbon chain, causing polymerization. Here is the basic cause of reconstruction of the molecule in rubber oxidation⁵.

Since $[O_2]$ and $[II]$ are practically constant, the speed of polymerization $d\Sigma/dt$ is proportional to the concentration of the radicals R ; i.e.

$$\begin{aligned} \frac{d\Sigma}{dt} &= p[R] = qK_3^m[n_0]^m = q \left(K \frac{W_i}{b_0 - W_i} \right)^m \\ &= q \left(K \frac{1}{\Delta t} \right)^m = q \left(\frac{dZ}{dt} \right)^m \quad (5) \end{aligned}$$

where $t = 0$, $\Sigma = 0$; therefore

$$\Sigma = \frac{qK^m}{(m-1)} \left[\left(\frac{W_i}{b_0 - W_{it}} \right)^{m-1} - \left(\frac{W_i}{b_0} \right)^{m-1} \right] \\ = \frac{qK^m}{(m-1)} \left[\left(\frac{1}{\Delta t} \right)^{m-1} - \left(\frac{1}{t_{\max}} \right)^{m-1} \right] \quad (6)$$

In summation, the speed of structural transformations dS/dt is equal to:

$$\frac{dS}{dt} = \frac{d\Sigma}{dt} - \frac{dZ}{dt} = q \left(K \frac{1}{\Delta t} \right)^m - K \frac{1}{\Delta t} \quad (7)$$

but the corresponding algebraic sum of elementary acts of structural transformation ΔS is equal to:

$$\Delta S = \Sigma - Z = \frac{qK^m}{(m-1)} \left[\left(\frac{1}{\Delta t} \right)^{m-1} - \left(\frac{1}{t_{\max}} \right)^{m-1} \right] - K \ln \frac{t_{\max}}{\Delta t} \quad (8)$$

When $t_{\max} = 1$, Equation (8) takes the form

$$\Delta S = \frac{qK^m}{m-1} \left[\left(\frac{1}{\Delta t} \right)^{m-1} - 1 \right] + K \ln \Delta t \quad (9)$$

We must note here that in the case of a butadiene-styrene polymer and vulcanizates of it, under certain conditions of oxidation, molecular destruction first prevails, followed by reconstruction (Figure 4); i.e., a break appears in the curve.

The extreme point reached in time t_e corresponds to a condition of equilibrium between the speeds of destruction and reconstruction; i.e.,

$$q \left(K \frac{1}{\Delta t_e} \right)^m = K \frac{1}{\Delta t_e}$$

from which

$$q = K^{1-m} \left(\frac{1}{\Delta t_e} \right)^{1-m} \quad (10)$$

Substituting the value q in (9), we get:

$$\Delta S = K \left\{ \frac{1}{m-1} \left[\left(\frac{\Delta t_e}{\Delta t} \right)^{m-1} - \Delta t_e^{m-1} \right] + \ln \Delta t \right\} \quad (11)$$

According to Bartenev³, the number of junctions in the vulcanization network per unit volume, N , is proportional to the quantity $E_{\infty}^{\frac{1}{2}}$. Consequently the change in the number of junctions during oxidation is equal to:

$$\Delta N = a(E_{\infty}^{\frac{1}{2}} - E_{\infty}^{\frac{1}{2}}(\text{initial})) = a\Delta(E_{\infty}^{\frac{1}{2}})$$

where a is the proportionality factor. Identifying ΔN and ΔS ,

$$\Delta(E_{\infty}^{\frac{1}{2}}) = \frac{K \Delta t_e / \Delta t - \Delta t_e^{m-1} + (m-1) \ln \Delta t}{a(m-1)} \quad (12)$$

Having measured the increment $\Delta(E_{\infty}^{\frac{1}{2}})$ for two periods of oxidation time t_1 and t_2 , we get:

$$\frac{\Delta(E_{\infty}^{\frac{1}{2}})_{(1)}}{\Delta(E_{\infty}^{\frac{1}{2}})_{(2)}} = \alpha = \frac{\Delta t_e / \Delta t_1 - \Delta t_e^{m-1} + (m-1) \ln \Delta t_1}{\Delta t_e / \Delta t_2 - \Delta t_e^{m-1} + (m-1) \ln \Delta t_2} \quad (13)$$

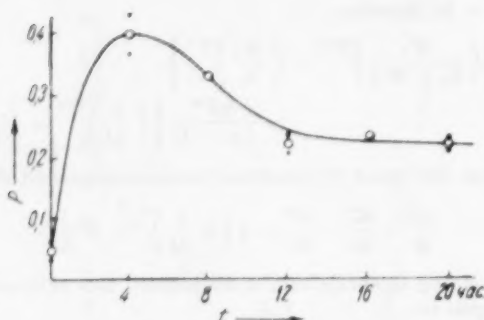


Fig. 4.—Change in the plasticity of the raw polymer in the process of oxidation at 120° C. The abscissa represents the time of oxidation in hours; the ordinate the plasticity P , measured by the method of Karrer.

By the use of (13) we can calculate the quantity m . We made the calculation for oxidation of an SKS-30 vulcanizate at 120° C. The mean value of m equaled 1.008. Substituting this value in (12), determining next the value K/a for t_0 , and knowing the original value of $E_{\infty}^{1/2}$, we constructed a theoretical curve of the change in this value during the oxidation of the vulcanizate (dotted line in Figure 2). A glance at this figure shows that the agreement between theory and experiment is very good.

It follows from (7) that

$$\frac{1}{\Delta t_c} = \frac{1-m}{\sqrt{qK^{m-1}}} = q^{1/1-m} K^{-1}$$

Note that the quantities q , K_0 , K_{∞} (and, consequently, K), as determining the speed of radical reactions, are almost independent of temperature; so indeed is the quantity m . Thus changes in temperature should have no appreciable effect on the quantity $1/\Delta t_c$; from which it follows that $\Delta t_c \cong \text{const}$.

This means that it is possible to calculate how the structure of rubber will change during the process of oxidation at a given temperature, according to data obtained at another temperature.

We calculated a theoretical curve for the change in $\Delta(E_{\infty}^{1/2})$ for the case of oxidation of the same specimen at 100° C (dotted line in Fig. 3). Its agreement with experimental values was quite satisfactory. Thus a quantitative relation was found between the quantities W_0 , t , and $\Delta(E_{\infty}^{1/2})$; i.e., a connection between the course of the chemical reaction and the change in mechanical properties was established.

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INHIBITION OF OXIDATION OF RUBBERS

RELATION BETWEEN MOLECULAR STRUCTURE AND THE EFFECTIVENESS OF INHIBITORS *

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As was pointed out in an earlier article¹, retardation of the oxidation of rubbers by secondary aromatic amines (arylamines) is due to rupture of the oxidized chain which takes place during the reaction of the initial oxygen-bearing active center of the hydrocarbon with the inhibitor molecule. The chemistry of this process evidently involves the stabilization of the active center at the expense of the most mobile hydrogen atom of the arylamine molecule, i.e., the hydrogen of the amino group, according to the following scheme:



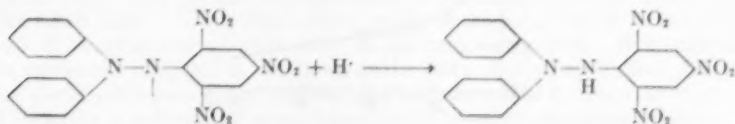
where R is the hydrocarbon radical, and A is the inhibitor radical.

It was established that an increase of the complexity of the molecule and the presence of substituents in *para*-position to the phenyl ring have a strong influence on the inhibiting action of arylamines. This phenomenon was interpreted as an indication of a relation between the reactivity of the molecule and its structure. Both of the means indicated for modifying the structure of the molecule must cause a change of the mobility of the hydrogen atom of the amine group, and, consequently, the rate of the inhibition reaction as well.

The purpose of the present study was an experimental investigation of the relation between the mobility of amine hydrogen and the molecular structure of arylamines. For this purpose, it was necessary to compare the mobility of hydrogen in various secondary amines. The method chosen was the comparison of the rates of reaction of amines with a substance which produces cleavage of the amine hydrogen.

The dehydrogenating agent used by the authors was α,α -diphenyl- β -picrylhydrazyl $\left[\begin{array}{c} R \\ | \\ R-N-N-R_1 \\ | \\ R \end{array} \right]$, which is a free radical able to exist for a long time

in air in either a crystalline state or in benzene solution². Hydrazyl is capable of reacting with amines, with removal of their amine hydrogen. The diphenylpicrylhydrazyl is thereby converted into the corresponding diphenylpicrylhydrazine.



* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Doklady Akademii Nauk SSSR*, Vol. 96, No. 6, pages 1187-1189 (1954).

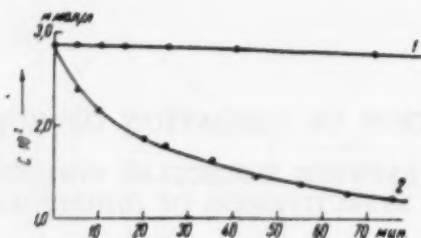


Fig. 1.—Kinetics of the reaction of α,α -diphenyl- β -picrylhydrazyl with *N*-methylphenyl-2-naphthylamine (1) and phenyl-2-naphthylamine (2) at 25° C. C = Concentration of hydrazyl. The ordinate indicates the $C \cdot 10^3$ values; the abscissa the time in minutes.

This conversion is accompanied by a change of the color of the system: the dark violet color characteristic of hydrazyl disappears, and the yellow color of hydrazine appears. Thus, the kinetics of separation of hydrogen from amines by hydrazyl can be studied colorimetrically.

First of all, it was necessary to prove that the reaction of hydrazyl with secondary arylamines actually is accompanied by removal of amine hydrogen. For this purpose we studied the kinetics of the reaction of hydrazyl with phenyl-2-naphthylamine and *N*-methylphenyl-2-naphthylamine. All the reactions took place in a benzene solution of chemically pure compounds. The consumption of hydrazyl was determined by a photoelectrocolorimeter, using a red filter, or by a spectrophotometer of wave length 590 $m\mu$. This region of the spectrum was chosen after a study of the spectra of absorption of hydrazyl and hydrazine in the visible range. The experiments were carried out in air, since a previous study had shown that the kinetic curves of the reaction of hydrazyl with phenyl-2-naphthylamine, photographed in a vacuum (10^3 mm. Hg) and in air, are completely superimposed. As is seen from Figure 1, the reaction of hydrazyl with an amine does not take place in the absence of amine hydrogen. On the other hand, the addition of phenyl-2-naphthylamine and hydrazyl to the system after the completion of the reaction of a small quantity of lead dioxide leads, after several days, to restoration of the violet color of hydrazyl. The preparation of hydrazyl from the corresponding hydrazine is based on this reaction.

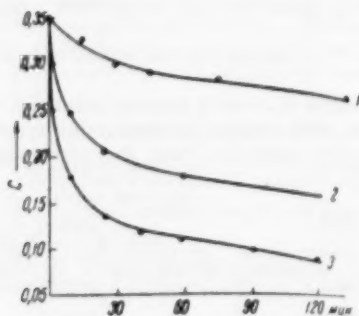


Fig. 2.—Kinetics of reaction of α,α -diphenyl- β -picrylhydrazyl with several amines at 40° C. 1. With diphenylamine. 2. With phenyl-2-naphthylamine. 3. With β,β' -dinaphthylamine. C = Concentration at hydrazyl. The ordinate indicates the C values; the abscissa the time in minutes.

The results presented, as well as data in the literature, attest to the fact that the reaction of diphenylpicrylhydrazyl with secondary arylamines is actually accompanied by removal of the hydrogen atom of the amino group.

The kinetic curves of the reaction of hydrazyl with secondary amines containing various numbers of aromatic rings in the molecule are shown in Figure 2. As is seen from the figure, the greater is the complexity of the molecule, the greater is the rate of the reaction, and consequently in this case, the mobility of the hydrogen of the amino group as well.

Comparing the results obtained with data on the inhibiting action of these compounds, it can be concluded that, in a number of secondary arylamines, the inhibiting action is determined by the mobility of the hydrogen atom of the amino group, which in turn depends on the complexity of the molecule.

Derivatives of phenyl-2-naphthylamine containing various substituents in *para*-position to the phenyl ring were studied next (see Figure 3). Comparison of the rates of reaction of hydrazyl with these compounds shows that the mobility of the hydrogen of the amino group increases with an increase of the

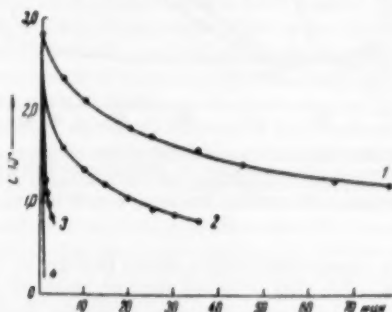


Fig. 3.—Kinetics of reaction of diphenylhydrazyl with derivatives of phenyl-2-naphthylamine at 25°C. 1. With phenyl-2-naphthylamine. 2. With *N*-methylphenyl-2-naphthylamine. 3. With *N*-methoxyphenyl-2-naphthylamine. 4. With *N*-hydroxyphenyl-2-naphthylamine. *C* = Concentration of hydrazyl. The ordinate indicates the $C \cdot 10^4$ values; the abscissa the time in minutes.

electrophilic properties of the *para*-substituted (the reaction with *N*-hydroxyphenyl-2-naphthylamine takes place instantaneously). The same law was observed by the authors with respect to the inhibiting action of these derivatives of phenyl-2-naphthylamine (*N*-methylphenyl-2-naphthylamine, which causes a somewhat shorter induction period of rubber oxidation than does phenyl-2-naphthylamine, is an exception).

Hence the *para*-substituents in the phenyl ring, as well as the conjugated double bonds, influence the inhibiting capacity of a compound, modifying the mobility of the hydrogen atom of the amino group. It is known that, in the induction period of rubber oxidation, the length of the oxidation chain is not equal to unity³. A partial decomposition or stabilization of the active peroxides takes place. These phenomena lead to some modification of the structure of the rubber hydrocarbon, even in the induction period. Naturally the more active the inhibitor is, the lower is the state of these structural changes. Thus, the effectiveness of an inhibitor can be determined by the rate of structural changes in rubber during oxidation in the presence of a given inhibitor.

The change of the high-elastic equilibrium modulus of heat vulcanizates of a rubber can serve as an index of the change in its structure. (A heat vulcanizate

is a rubber hydrocarbon which forms a spatial network at 200° C in 40–80 minutes.) The high-elastic equilibrium modulus E of a vulcanizate is related to the number of unions in its network in a unit volume N by the simple equation⁴:

$$E = kN^{\frac{1}{2}}$$

The equilibrium modulus was determined by the method of after-effects. The change of the equilibrium modulus during oxidation of heat vulcanizates of sodium-butadiene rubber at 130° C in the presence of various inhibitors is shown in Figure 4, where the arrows show the moment of destruction of the heat vulcanizates.

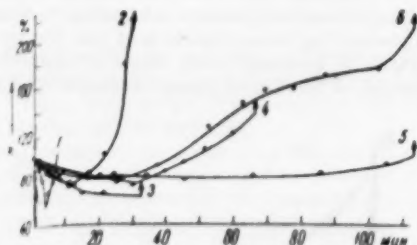


Fig. 4.—Change of equilibrium high-elastic modulus (M) of heat vulcanizates during aging (130° C) in the presence of various inhibitors: 1. Diphenylamine. 2. Phenyl-2-naphthylamine. 3. *N*-Methylphenyl-2-naphthylamine. 4. *N*-Methoxyphenyl-2-naphthylamine. 5. *N*-Hydroxyphenyl-2-naphthylamine. 6. β -Dinaphthyl-*N*-phenylenediamine. The ordinate indicates the modulus (M) values; the abscissa the time in minutes.

Comparison of the experimental data shown in Figures 2, 3, and 4, and also the data on oxidation inhibition obtained earlier¹, show that the rate of structural changes in vulcanizates during inhibited oxidation depends directly on the strength of the N—H bond in the arylamine molecule. The more easily cleavage of the hydrogen from the inhibitor molecule takes place, the greater is the effectiveness of the inhibitor as a protective agent.

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EFFECT OF OXIDATION OF RUBBER ON THE KINETICS OF ITS SWELLING *

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The diffusion of a solvent through a high polymer is caused by an aggregate development of intermolecular forces and a change in the entropy of the system. Many authors have studied the equilibrium state of a swollen high polymer placed in a solvent from this standpoint¹. The influence of the nature of molecular reaction on the kinetics of swelling has been recognized in some works, but this aspect of the question has been treated less thoroughly. The study of the rate of swelling of various rubbers in various solvents has required, first of all, the development of a method which would make it possible to measure the change of volume or weight of a swollen specimen, without considering the effect of reaction with oxygen.

Since the processes of structure formation and destruction of the polymer, which progress concurrently with swelling, and which are caused by the aggressive action of atmospheric oxygen, can distort the picture observed, appropriate experiments were set up in order to account for the influence of oxygen. In order to explain the effect of oxidation of the rubber hydrocarbon on the kinetics of swelling of the latter, the kinetics of swelling of rubbers were plotted at various periods of heat aging. The rate of swelling of rubbers both with and without age resistor was also determined.

The kinetic curves of swelling of butadiene-styrene rubber at various periods of heat aging in an air thermostat at 80° are shown in Figures 1 and 2. In setting up this experiment, a solvent was chosen in which the absolute values of the degree of swelling would not be too small and, at the same time, the oxidized product would swell more than the unoxidized one. For this purpose, the kinetics of swelling of SKS-30 rubber was studied at various periods of aging in ethylmethyl ketone, in ethyl alcohol, and in methyl alcohol. Since the specimens which were aged swelled infinitely in ethylmethyl ketone, it was necessary to abandon this solvent. The degree of swelling of SKS-30 rubber at various stages of aging was considerably less in ethyl alcohol than in methyl alcohol; however, the nature and distribution of the swelling curves remained about the same. The experimental method consisted of cutting specimens, 3.5 × 3.5 mm., from various parts of a sheet of rubber and placing them in tall containers with tight covers, filled with 5 ml. of solvent.

The degree of swelling Q was obtained from the equation: $Q = \frac{P_H}{P_C}$, where P_H is the weight of a swollen specimen, and P_C is the weight of the specimen after elimination of the solvent.

The study of the swelling curves of SKS-30 rubbers at various stages of aging in methyl alcohol shows that unaged rubber reaches a maximum swelling

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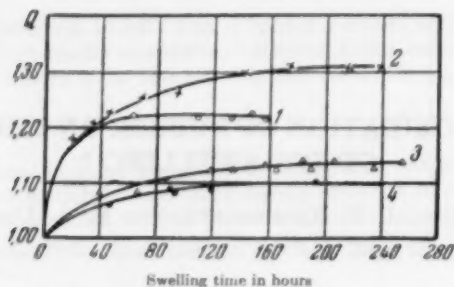


FIG. 1.—Kinetics of swelling of SKS-30 rubber at various periods of heat aging in ethyl alcohol: 1—before aging; 2—after 8 days; 3—after 15 days; 4—after 23 days.

in methyl alcohol in 30 hours, after which the swelling shows no appreciable change of Q for 110 hours.

All aged rubbers show a continuously increasing degree of swelling in methyl alcohol. The kinetic curves of swelling of these specimens are more even, and pass into a straight line after about 200 hours of swelling.

A sharp increase of degree of swelling of rubber in methyl alcohol is observed after 8 days' aging, followed by an even sharper decline after 15 days. Further increase of the aging period to 23 days has little effect on the degree of swelling. A similar law is observed in rubbers swollen in ethyl alcohol.

This change of the kinetics of swelling and absolute values of the degree of swelling evidently indicates processes of destruction, structure formation, and accumulation of polar groups in butadiene styrene rubber during aging. During the first 8 days evidently destruction of the molecular chains under the influence of oxygen predominates, along with the accumulation of polar atomic groups. Later on, the process of destruction commences with cross-linking of the rubber molecules and with formation of a spatial network. The formation of cross-linkages diminishes the mobility of the chain molecules of the rubber; as a result, certain configurations become impossible for them. Changes in the structure of the rubber also lead to a decrease of the entropy of swelling.

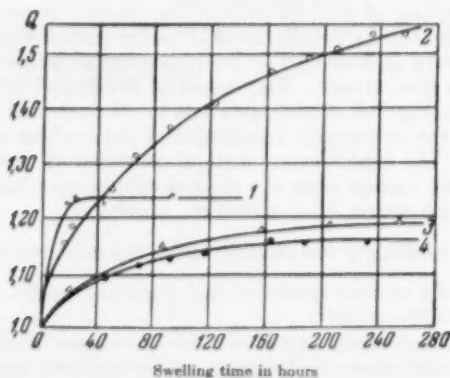


FIG. 2.—Kinetics of swelling of SKS-30 rubber at various periods of heat aging in methyl alcohol: 1—before aging; 2—after 8 days; 3—after 15 days; 4—after 23 days.

Further increase of the aging period of butadiene-styrene rubber evidently does not lead to any essential change in its structure; hence, the degree of swelling of a specimen in the third aging period (curve 4) is only slightly less than that of a specimen in the second aging period (curve 3).

It should be noted that these results correspond well to the data on plasticity (Defo) of these rubbers.

Here are the values of plasticity (Defo) for butadiene-styrene rubbers of various aging periods.

before aging	350
8 days' aging	1850
15 days' aging	2000
23 days' aging	2200

The sharp decrease of plasticity after 8 days' aging reflects the thorough destruction processes, which later on are more and more counterbalanced by processes of union of the destroyed molecules.

This peculiar process of structure formation has a slight effect on plasticity, since it leads to the formation of side-chain molecules.

Thus, the process of oxidation destruction and the accumulation of polar products of oxidation in butadiene-styrene rubber is accompanied by an increase of the degree of swelling in methyl and ethyl alcohol, and the process of structure formation, by a decrease of the swelling maximum. The influence of the oxidation of rubber on the kinetics of swelling is seen even more graphically in testing butadiene-styrene rubbers when the age resistor and soluble byproducts of oxidation are removed. Specimens of butadiene-styrene rubber were extracted with methyl alcohol, dried in a vacuum, and again swelled in methyl alcohol. The kinetic curves of swelling of butadiene-styrene rubber containing Neozone-D (unextracted) and without age resistor (extracted) are shown in Figure 3. These data show clearly how the nature of swelling of rubber changes after the substances which protect it from oxidation are removed. Rubber which was not previously extracted reaches a swelling maximum in the first 20 hours, after which the degree of swelling does not change. If the age resistor is extracted from the rubber, the degree of swelling will continuously increase and the swelling maximum will be reached only after 320 hours.

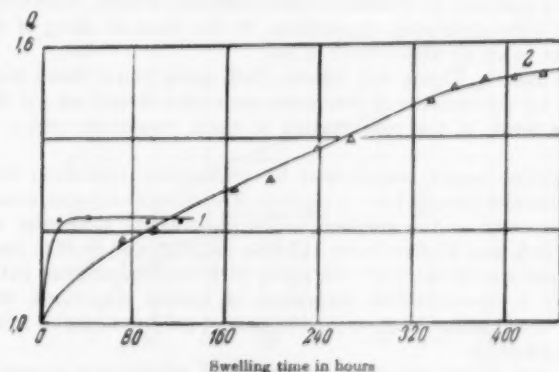


FIG. 3.—Kinetics of swelling of SKS-30 rubber in methyl alcohol before (curve 1) and after (curve 2) 10 days' extraction in methyl alcohol.

It is possible to study the influence of the structural changes which take place in butadiene-styrene rubber during heat aging and their effect on swelling in methyl alcohol by comparing the molecular weights. As was shown by Dogadkin², the value of the molecular weight, determined by any method, is insufficient to permit any unequivocal conclusions about the changes which take place in the rubber. For this reason the necessity arose for obtaining the characteristics of the molecular weights determined by viscometry or light-scattering. The methods of viscosity and light-scattering of solutions were used in the determination of the molecular weights of butadiene-styrene rubbers after various periods of aging. The values of the viscometric molecular weight were calculated according to the formula:

$$[\eta] = kM^{\alpha},$$

where $[\eta]$ is the characteristic viscosity, M is the molecular weight; k is a constant for solutions of butadiene-styrene copolymer, equal to 5.4×10^{-4} ; and α is a constant equal to 0.66.

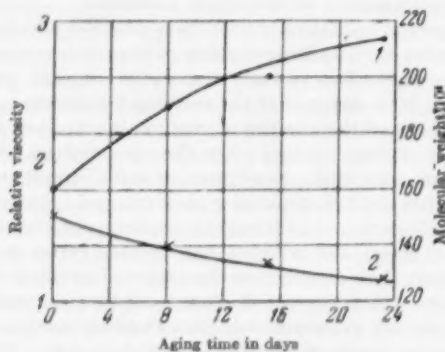


FIG. 4.—Change of molecular weight, determined by light scattering and relative viscosity of solution of SKS-30 rubber, as related to aging time: 1—molecular weight; 2—relative viscosity.

In Figure 4 is shown the relation of the molecular weight, determined by the viscosity and light-scattering of solutions, to the time of aging of butadiene-styrene rubber in an air thermostat at 80°.

From the data in Figure 4 it follows that aging under these conditions is accompanied by an increase of the mean molecular weight and a decrease of viscosity as a result of the combination of chain fragments into a side-chain structure.

The molecular weight, determined by viscometry, decreased because the side-chain molecules formed have a smaller effective volume and, consequently, reduce the viscosity of the solution. The viscometric molecular weights of rubbers aged 0, 8, and 15 days were 217,000, 103,000, and 64,000, respectively.

Thus we are convinced that the aging of butadiene-styrene rubber is accompanied by a corresponding formation of spatial structures, which at a certain stage of oxidation leads to an increase of gel fraction and a decrease of the degree of swelling.

In Figure 5 is shown the graphic relation of gel-fraction content to aging time. This relation shows that, starting from 15 days of heat aging, a pro-

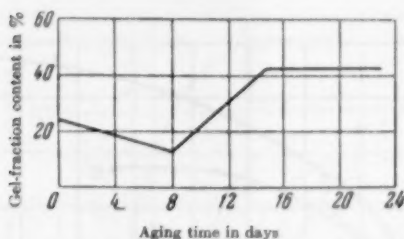


Fig. 5.—Change of gel-fraction content of SKS-30 rubber as related to aging time.

nounced cross-linking of the chain molecules is observed, evidently causing a sharp decrease of the degree of swelling.

Since the oxidation of butadiene-styrene rubber is accompanied by a very uneven (in the sense of its influence on aging) change of structure, the influence of oxidation on swelling was also examined for the case of natural rubber.

Figures 6 and 7 show the kinetics of swelling of various specimens of natural rubber in methyl alcohol, as well as the kinetics of swelling of smoked sheet aged 9 and 20 days at 80°.

The kinetic curve of swelling of the third specimen which has a monotonic rising form, is noteworthy. This curve reflects the continuous oxidation of the polymer during swelling; consequently, the degree of swelling rises all the time. It will be shown later that specimen 3 actually resists the action of oxygen poorly, so that it reacts slightly with the oxygen dissolved in the methyl alcohol during swelling. This leads, on the one hand, to an accumulation of polar oxidized groups and, on the other, to the formation of side-chain rubber molecules, which, in turn, causes an increase in the degree of swelling of the rubber. In order to confirm the truth of these assumptions regarding the oxidation processes which take place during swelling of rubber, a special experiment on the swelling of natural rubber, with and without age resistor, was arranged.

The rubber was dissolved in benzene, reprecipitated, and the pure rubber hydrocarbon obtained, containing no age resistor, was swelled in methyl alcohol. All the steps in the preparation of a pure natural-rubber hydrocarbon were

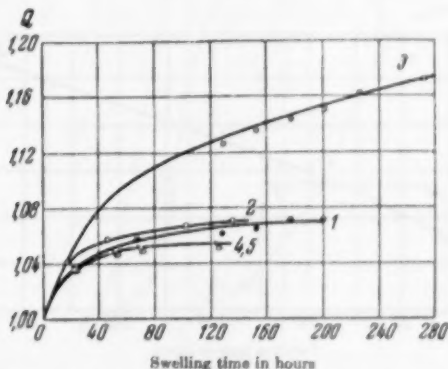


Fig. 6.—Kinetics of swelling in methyl alcohol of various specimens of smoked sheet.

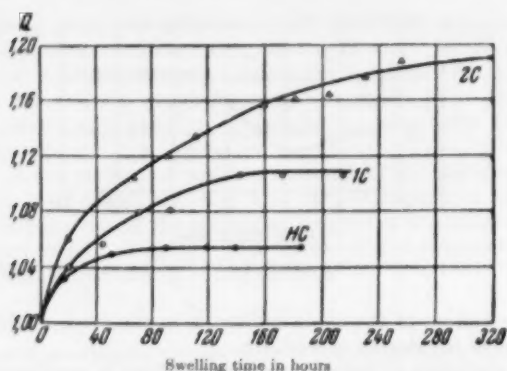


FIG. 7.—Kinetics of swelling of smoked sheet, heat-aged for various periods: 1C—9 days; 2C—20 days.

carried out in an atmosphere of purified nitrogen. Data for the kinetics of swelling of a pure hydrocarbon and rubber containing natural protective substances are shown in Figure 8. These data confirm the assumptions made above. The swelling curve of the pure hydrocarbon is even, gradually passing into a straight line, while the swelling maximum could not be reached, although the original rubber reaches the swelling maximum in about 70 hours.

A similar law is observed, as can be seen in Figure 7, in rubber subjected to heat oxidation for a certain time. The kinetic curves of swelling of natural rubber, unaged and aged for 9 and 20 days at 80°, are shown in Figure 7. The rubber whose molecules did not undergo the destructive action of oxygen has a lower degree of swelling than that which, after aging, had a lower molecular weight. Furthermore, the swelling curve of the specimen aged 20 hours is monotonic and rising, indicating that the swelling process is accompanied by absorption of oxygen by the rubber. This is due to the fact that preliminary aging led to the union of the rubber with its natural age resistors. It will be shown below that this rubber actually has hardly any induction period during

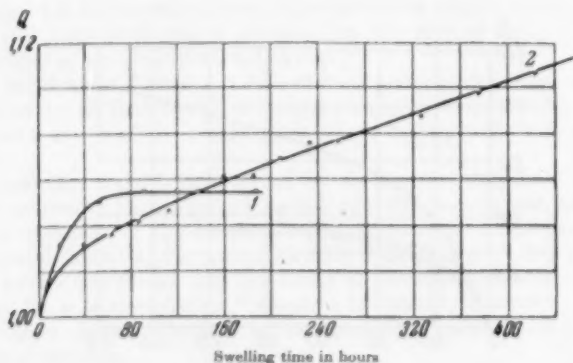


FIG. 8.—Kinetics of swelling of natural rubber in methyl alcohol: 1—smoked sheet containing natural substances; 2—pure smoked-sheet rubber hydrocarbon.

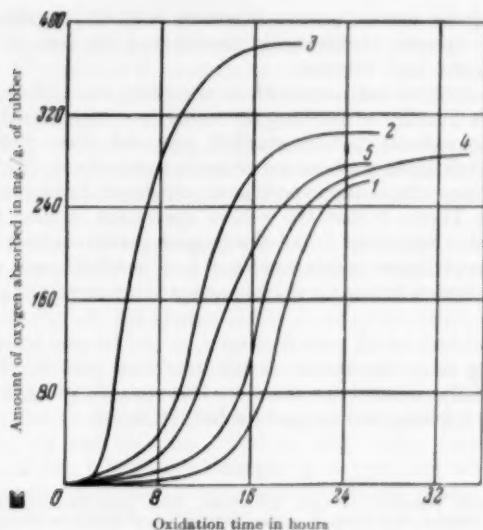


FIG. 9.—Kinetics of oxidation of various specimens of smoked sheet with molecular oxygen at 143° .

oxidation at 143° , while the specimen which was not aged first has a 14-hour induction period at the same temperature.

The increase of the degree of swelling of natural rubber with aging must be ascribed to the influence of the accumulating polar atomic groups. The ac-

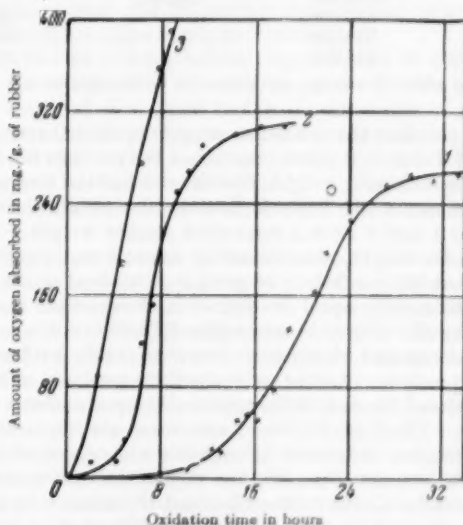


FIG. 10.—Kinetics of oxidation of smoked sheet aged for various periods at 143° : 1—aged 9 days; 2—aged 20 days; 3—not aged.

cumulation of polar atomic groups increases both the equilibrium degree of swelling (at the expense of the energy factor) and the rate of diffusion of the solvent through the high polymer.

In order to confirm our assumptions regarding the influence of oxidation processes on the kinetics of swelling of rubber, we determined the kinetics of oxidation of the natural rubbers studied, and also their molecular weights. The kinetics of oxidation was measured manometrically at 143° in a Dufraisse apparatus. The results of the experiments are shown in Figures 9 and 10.

It is seen in Figure 9 that the rubber specimens studied have a varying induction period. Specimen 1 had the longest period—about 12 hours; then specimen 4, about 8 hours; specimens 5 and 2, about 4–6 hours, and, finally, the third specimen, which evidently is less protected by natural age resistors than the others.

As for the rubbers which were first aged, as can be seen from Figure 10, the longer the aging time, the shorter is the induction period. Rubber aged 20 days has practically no induction period. Rubber aged 9 days has an induction period of about 4 hours, and unaged rubber, 10 hours.

TABLE 1

MOLECULAR WEIGHT OF 1ST, 2ND, 3RD, 4TH, AND 5TH SPECIMENS OF SMOKED SHEET, UNAGED SMOKED SHEET, AND SMOKED SHEET AGED FOR 9 AND 20 DAYS AT 80°, DETERMINED BY VISCOSITY, OSMOMETRY AND LIGHT SCATTERING

Rubber specimen	Viscosity method	Osmometry method	Light-scattering method
1	330,000	270,000	
2	240,000	270,000	
3	160,000	180,000	
4	270,000	310,000	
5	310,000	290,000	
NA	380,000		380,000
1A	310,000		280,000
2A	210,000		100,000

Notes: NA—unaged rubber; 1A—rubber aged 9 days; 2A—rubber aged 20 days.

We shall now consider the molecular weights of the natural rubbers studied. From the data of Table 1, it can be seen that the rubbers fall in the following order according to molecular weight: Specimen 5 has the largest mean molecular weight. Specimen 4 also has a high molecular weight determined osmotically. Specimens 1 and 5 have a somewhat smaller weight. Specimen 3 has the lowest molecular weight, determined by osmotic and viscometric methods.

We assume that the conditions of genesis of rubbers in the plant assure in all cases an approximately equal development of side-chain molecules, if there are any of these at all. For this reason the difference in the molecular weight, determined by osmosis and viscometry, is caused chiefly by the degree of polydispersion of the product. Accordingly, the fifth specimen must be considered the least polydispersed, because it has practically equal osmotic and viscometric molecular weight. The first and fourth specimens are the most polydispersed; their molecular weights measured by osmosis and viscometry, vary widely. All these considerations are of importance only in the case where the relation of sol and gel fractions for all the rubbers is about the same. As is seen from the data in Table 2, the gel-fraction content in smoked-sheet specimens varies between 3 and 6 per cent, which, it seems to us, can have no essential influence

on either the molecular weights of the dissolved fraction or the value of the other physical-chemical characteristics of the rubber.

The greatest difference in the molecular weights of the rubbers is most probably the result of the action of oxygen. In this connection, specimen 3, which has a high content of polar oxidized groups, has a lower molecular weight. Specimens 4 and 5, which have the highest molecular weights, reflecting their slight oxidation, show the lowest degrees of swelling in methyl alcohol; their swelling curves are lower than all the others. Specimen 1 occupies an intermediate position.

Thus, the experimental results reproduced support the assumption that a definite relation exists between the degree of oxidation of natural rubber and the value of the swelling maximum in a polar solvent. The higher is the degree of oxidation of the rubber, the greater is the value of the swelling maximum in methyl alcohol.

It should be noted that swelling in a polar solvent excludes partial solubility of a polymer, so that the changes in a rubber due to the action of oxygen and the differences in the molecular characteristics are not affected by any concurrent processes of swelling and solution. Besides this, under these experimental conditions, non-rubber ingredients containing oxygen are absorbed by the methyl alcohol, so that the value of the swelling obtained characterizes directly the properties of the rubber hydrocarbon. Numerous experiments on the

TABLE 2
GEL-FRACTION CONTENT OF SMOKED SHEET SPECIMENS STUDIED

Specimen	1	2	3	4	5
Gel-fraction in %	5.9	4.3	2.5	3.7	5.3

swelling of natural rubber have shown that, on the average, about 3 per cent by weight of the specimen goes into the methyl alcohol, that is, a large part of the low-molecular non-rubber ingredients are washed out.

Swelling of rubber in a polar solvent can be used to obtain information about the resistance of rubber to attack by oxygen. In this case, the swelling process must be regarded as a quick test of the resistance of rubber to aging. This method has the advantage over those known before (aging in a thermostat, aging in an oxygen bomb) in that it proceeds quite rapidly at room temperature, and, in obtaining data on the behavior of rubber during storage, it is not necessary to determine the temperature coefficients of the reactions which accompany aging.

During swelling, the molecules of the solvent are diffused in the molecules of the polymer, thus facilitating the access of the oxygen dissolved in the solvent to the most active parts of the rubber molecules, i.e., the double bonds.

Inasmuch as the absorption of oxygen does not take place instantaneously, the degree of swelling also increases continuously during the entire contact between the rubber and the swelling agent. This leads to a practically linear segment on the kinetic curve of swelling of rubber during the reaction with oxygen beyond the region characterizing the rapid diffusion process; this reflects a slow change in the degree of swelling as a result of the oxidation processes.

If a rubber is well protected by natural age resistors, the absorption of oxygen at ordinary temperatures proceeds very slowly, so that the phenomenon described is not observed. The swelling maximum is reached in a relatively short time, and after that the degree of swelling does not change.

Thus, according to the form of the kinetic curves of swelling shown in Figures 1-8, it is possible to determine both the degree of oxidation of the rubbers studied or the functionally related size of the molecular chain, and their ability to resist oxidation.

The absolute values of the swelling maximum (because of the absence of oxidation processes) depend on the molecular characteristics of the high-polymer, such as the molecular weight, degree of polydispersion, and proportion of gel and sol fractions. Furthermore, the degree of swelling is also determined by the molecular reaction between the solvent and polymer. From this standpoint, the composition of the impurities which go into solution during swelling, as well as the degree of oxidation of the rubber, are far from unimportant.

CONCLUSIONS

1. Swelling of rubber during reaction with oxygen is described by a kinetic curve. After a sharply rising segment, corresponding to the diffusion of the solvent, the curve has a practically linear segment, reflecting a slow change of the degree of swelling due to the oxidation processes which accompany swelling.

2. The swelling maximum of rubber in a polar solvent when the oxidation effect is disregarded, corresponds to the molecular weight, degree of dispersion, and other structural properties of the rubber. The slope of the linear segment of the kinetic curve of swelling can serve as a characteristic of the resistance of the rubber to oxidation.

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DIFFUSION OF ANTIOXIDANTS IN RUBBER *

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The study of the diffusion of polymers in order to determine the size and shape of the macromolecules in solutions has been the subject of numerous recent works. Considerably fewer studies have been devoted to the problem of the diffusion of low-molecular substances dissolved in polymers, and the existing works in this field refer principally to gas-polymer systems.

It is also known that the rate of diffusion in polymers of solid and liquid low-molecular compounds governs in a number of cases the kinetics of processes of great practical importance. In particular, the kinetics of a process as important to the rubber industry as the oxidation of rubber is, to a large degree, related to the rate of diffusion of antioxidants and other soluble ingredients in the rubber.

Rubber as a diffusion medium is distinguished from liquids and solid crystalline substances by certain properties which are governed by the characteristic heat movement of the macromolecules. Thus, Brün¹ showed that Einstein's equation cannot be applied in the case of diffusion in rubber, and Barrer² developed a theory of diffusion of gases in rubber, according to which the presence of an activation zone is necessary for the initial process of diffusion.

The present study concerns the diffusion of certain solid antioxidants dissolved in rubber (phenyl-2-naphthylamine, dinaphthylamine, and dinaphthyl-phenylenediamine).

The principle of Fürt's micromethod was used to determine the coefficients of diffusion. Since the substances chosen for investigation form colorless solutions in rubber, the position of the concentration limit was determined by the intensity of luminescence during illumination with filtered ultraviolet light.

Two pressed sheets of rubber, each 0.5 mm. thick, one containing the dissolved substance, were clamped tightly on the microscope slide, previously marked with India ink. The prepared mixtures were placed in glass ampules, which were filled with nitrogen, sealed, and kept for the given period in an ultrathermostat at different temperatures.

The coefficient of diffusion D was calculated on the basis of the change of the distance x between the initial limit and the concentration limit, which corresponds to the dilution v in the time t according to the relation:

$$D = \frac{x^2}{t} \cdot \frac{1}{4[\varphi(1 - 2/v)]^2}$$

where φ is the inverse function of the integral of errors of Gauss.

The experiments were carried out with a control solution, of dilution $v = 32$. The linear nature of the relation of x^2 to t (see Figure 1) indicates that the

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Doklady Akademii Nauk SSSR*, Vol. 98, No. 4, pages 611-612 (1954).

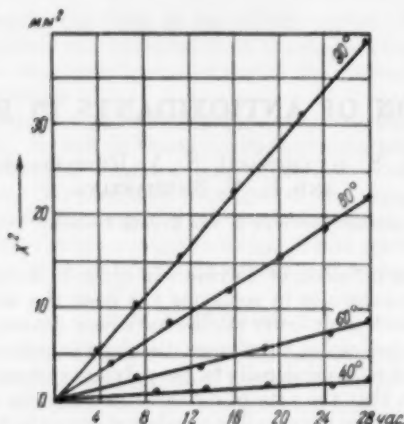


Fig. 1.—Relation of x^2 to time of diffusion. The system: phenyl-2-naphthylamine and polybutadiene. The abscissa indicates the time in hours.

system conforms to Fick's equation. By determining D for various original concentrations of diffusing substances, it can be established that the rate of diffusion in rubbers is related in a simple way to the concentration, and the value of D increases with an increase of concentration.

Thus it must be concluded that the diffusion of solid substances dissolved in rubber follows Fick's law, taking into account the concentration relation of the diffusion coefficient:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right)$$

The temperature dependence of D of the substances studied in polybutadiene is shown in Figure 2. The relation $\log D(1/T)$, constructed according to the

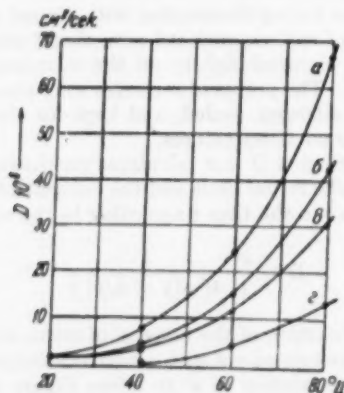


Fig. 2.—Coefficient of diffusion as a function of the temperature for phenyl-2-naphthylamine (a), dinaphthylamine (b), sulfur (c), and dinaphthylphenylenediamine (d) in polybutadiene. The ordinate indicates the diffusion coefficient $D \times 10^9$ in sq. cm. per second; the abscissa the temperature.

data in Figure 2, is linear for the given temperature range, while the activating energy of diffusion of phenyl-2-naphthylamine in polybutadiene is about 12,500 calories per mole.

The influence of the molecular structure of rubber on the value of D is shown for the diffusion of phenyl-2-naphthylamine in a butadiene-acrylonitrile copolymer WSKN-26), and polyisobutylene (see Figure 3). The order of dis-

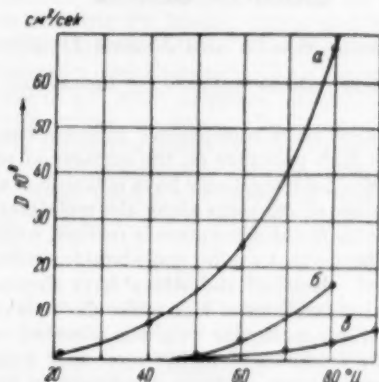


FIG. 3.—Coefficient of diffusion as a function of the temperature of phenyl-2-naphthylamine in polybutadiene. (a), a butadiene-acrylonitrile copolymer (SKN-26) (b), and polyisobutylene (c). The ordinate indicates the diffusion coefficient $D \times 10^8$ in sq. cm. per second; the abscissa the temperature.

tribution of the rubbers according to the value of D for a phenyl-2-naphthylamine-rubber system is maintained, just as in the case of diffusion of gases in these rubbers².

The value of the coefficient of diffusion of phenyl-2-naphthylamine in polybutadiene (2.10^{-8} sq. cm. per sec.) is approximately two orders lower than that of the diffusion of oxygen in polybutadiene (1.5×10^{-6} sq. cm. per sec.) and this may explain the lower activity of antioxidants in rubber than in liquids, where the values of the coefficients of diffusion of oxygen and antioxidants are of the same order.

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ADSORPTION OF ELASTOMERS ON CARBON BLACK *

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During the past three years considerable progress has been made in the study of adsorption of high polymers on the surfaces of solids from solution. A number of experimental investigations¹ have established that linear polymers are adsorbed at a number of segments along the molecular chain and that an apparent saturation value of the adsorption is reached with increasing concentration, leading to isotherms that exhibit considerable similarity with the classical Langmuir isotherm². Kolthoff and others³ have shown that poor solvents favor adsorption and that fractions of high molecular weight are adsorbed preferentially. Polymer of low molecular weight is adsorbed more rapidly, but is eventually replaced by fractions of higher molecular weight. Kolthoff and Gutmacher⁴ also observed some evidence of adsorption hysteresis in rubber-carbon black systems. Preferential adsorption effects have also been described by Goldfinger and others⁵, who, in addition, furnished an estimate of the thickness of the adsorbed layer⁶. Theoretical explanation for many of these effects has recently come from a detailed statistical mechanical treatment of polymer adsorption by Frisch, Simha, and Eirich⁷.

It is somewhat surprising that the adsorption of elastomers on reinforcing fillers from solution has received so little attention as a possible tool for the investigation of the polymer-filler interaction responsible for reinforcement. The reason for this appears to lie in the emphasis placed by many workers on the incomplete desorption effect observed when mill-mixed unvulcanized stocks are extracted with solvents. The well known bound rubber phenomenon observed in this instance⁸ is large and shows some correlation with reinforcement, mainly because the effect is surface area-dependent⁹. The fact that adsorption from solution is small when compared to bound rubber, particularly when a good solvent is used, has led some authors to consider the two effects as essentially separate phenomena¹⁰ and to dismiss solution adsorption as without interest in reinforcement.

The present investigation was undertaken with the twofold objective of determining if adsorption isotherms of elastomeric molecules of carbon black are capable of detecting an activity effect, divorced from the influence of surface development, which would show correlation with reinforcement, and secondly of establishing the interrelation between adsorption and desorption, i.e., bound rubber. The carbon blacks selected for this research (Table I) represent a fairly complete cross-section of rubber carbons as to both type and particle size. *n*-Heptane was chosen for all adsorption experiments, for the reason that a relatively poor solvent, which would favor large adsorption for all three rubbers, was desired.

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EXPERIMENTAL

Carbon blacks.—The electron microscope and nitrogen adsorption surface areas of the carbon blacks are listed in Table I. These values were obtained on the identical lots of black used in the present investigation. Preliminary adsorption experiments established the necessity for removal of adsorbed tars from the carbon blacks as a means for improving reproducibility of results. All carbons were, therefore, extracted with benzene for 72 hours in Soxhlet extractors, except the SRF and FT blacks, which were extracted 96 and 144 hours, respectively. The extracted blacks were dried at 70° C in vacuo and stored in a vacuum desiccator over Drierite. All carbon blacks were in pelleted form with the exception of FT, SRF, acetylene, and SAF II and III.

Polymers.—The cold rubber employed (X-672) was a 75/25 butadiene-styrene copolymer of 48 Mooney prepared in a sugar-free recipe at 41° F. The polymer was purified by Soxhlet extraction with the azeotropic mixture of ethyl alcohol and toluene. After drying, the extracted rubber was dissolved in toluene, reprecipitated with an excess of methanol, and vacuum-dried to con-

TABLE I
SURFACE AREA OF CARBON BLACKS

Carbon black type	Surface area	
	N ₂ adsorption (BET) (sq. m./g.)	Electron microscope (sq. m./g.)
FT	13.7	17
SRF	27.6	35
FEF-I	45.6	65
FEF-II	47.8	65
Acetylene	56.0	65
HAF	75.1	94
Graphon	93.7	113
EPC	114.2	89
SAF-I	142.6	138
SAF-II	153.4	129
SAF-III	184.2	123

stant weight at 50° C. The purified copolymer had an inherent viscosity in benzene of 1.86. The Butyl rubber (GR-I-18) was purified in similar fashion, except that it was dissolved in benzene rather than toluene. Inherent viscosity in benzene was 0.86. The natural-rubber sample was prepared by extracting masticated No. 1 smoked sheet with acetone for 72 hours, vacuum-drying at 40° C, dissolving in benzene, precipitating with methanol, and again drying at 40° C in vacuo. The inherent viscosity of the purified rubber was 2.38. All purified polymers were stored in the dark in a vacuum desiccator.

Procedure.—Sodium-dried *n*-heptane (Phillips pure grade) was used as the solvent in all adsorption experiments. The solvent and various quantities of purified polymer were charged into clean, dry, crown-capped 6-ounce beverage bottles, purged with dry nitrogen, and tumbled end over end in a constant temperature bath set for 30° C until all of the polymer dissolved. The bottles were removed from the bath and the carbon black was charged. After another purging with nitrogen, the bottles were resealed, returned to the bath, and allowed to tumble for the desired length of time (see section on rate of adsorption). The equilibrium concentration of rubber in the solution phase was determined gravimetrically by centrifuging out the black and evaporating an

aliquot in a tared aluminum foil moisture dish. In a few instances, complete removal of black by centrifuging was not possible, and the solutions analyzed contained small amounts of carbon black. A correction was applied by determining the carbon black content by digesting the rubber with hot nitric acid, diluting with water, filtering, and dissolving the nitration products with acetone. After numerous washes with acetone, the carbon black was dried at 75° C in vacuo and weighed.

Desorption isotherms were obtained by removing a portion of the supernatant liquid from the bottles at equilibrium and replacing the solution withdrawn with fresh solvent. The bottles were returned to the bath, and the first desorption point was taken no earlier than 48 hours after dilution. This procedure was repeated for further desorption points.

Calculation of isotherms.—The isotherms were calculated from the experimental data as follows.

Let W_0 be the weight of polymer charged, ρ the density of the rubber, and V_0 the volume of solvent in the charge. If the concentration of the solution at the point of apparent equilibrium is C_1 (grams per volume of solution), the weight of rubber adsorbed will be:

$$a_1 = W_0 - c_1 V_0 / (1 - c_1 / \rho) \quad (1)$$

In the process of determining c_1 , w_1 grams of rubber and v_1 ml. of solution have been removed. Let u_1 be the volume of solvent added for the determination of the first desorption point. The amount of rubber, W_1 , and the volume of solvent, V_1 , present at this stage are:

$$W_1 = W_0 - w_1 \quad (2)$$

and

$$V_1 = V_0 + u_1 - (v_1 - w_1 / \rho) \quad (3)$$

If the concentration for the first desorption point is c_2 , the corresponding adsorption is:

$$a_2 = W_1 - c_2 V_1 / (1 - c_2 / \rho) \quad (4)$$

or, similarly, for the $(n - 1)$ th desorption point:

$$a_n = W_{n-1} - c_n V_{n-1} / (1 - c_n / \rho) \quad (5)$$

In the preceding calculations, all volumes have been assumed to be additive.

Whenever carbon black was present in the solution analyzed, the adsorption points were calculated by a successive approximation method. In the first approximation the black was neglected and a_1 calculated by Equation 1, treating the black as if it were rubber. In the second approximation a new concentration, c'_1 , was calculated:

$$c'_1 = (w_1 - b - a_1 b / W_b) / (v_1 - b / \rho_b) \quad (6)$$

where w_1 is the solid content in volume v_1 , b is the weight of black in v_1 , W_b is the total weight of black in the charge, and ρ_b is the density of the black. The new concentration was used to calculate a new adsorption, a_1 , and the entire process was repeated until the values of c_1 and a_1 did not change on further approximation. Usually no more than three approximations were necessary, since the quantity of dispersed black was small to start with.

Extraction experiments on adsorbed rubber.—Samples of carbon black plus adsorbed rubber were transferred directly into tared extraction thimbles, weighed and extracted with the appropriate solvent in a Soxhlet apparatus for 72 hours. After extraction the black was dried and weighed, and the polymer content in the extract determined. The quantity of adsorbed rubber extracted is readily calculated. All values were corrected for rubber in the solution trapped between carbon black particles.

Bound-rubber determinations on mill-mixed carbon black-rubber masterbatches were carried out on 0.4-gram samples enclosed in stainless-steel wire screen cages, using 80 ml. of reagent grade benzene as the solvent. Results were expressed as percentage of polymer insolubilized. In the determination of the critical loading for coherent carbon gel formation, small samples of the masterbatch were immersed in benzene, allowed to swell for 30 minutes, and filtered through No. 1 Whatman filter paper. A clear filtrate was considered evidence that a coherent gel had been formed. This measurement is greatly dependent on the time elapsed between milling and testing. The samples were, therefore, tested periodically until no more changes were observed on further resting of the carbon-rubber mixes at room temperature. This required a total of approximately 30 days.

TABLE II
COMPOUNDING RECIPES

GR-S-101	100	—	—
No. 1 smoked sheet	—	100	—
GR-I-17	—	—	100
Carbon black	50	50	50
Zinc oxide	3	4	5
Stearic acid	—	3	1
Sulfur	1.75	2	2
Santocure	1.10	0.5	—
Tuads	—	—	1
Captax	—	—	1
Cure	45 minutes at 307° F		

Heat treatment of carbon-rubber masterbatches was carried out in an atmosphere of prepurified nitrogen.

Compounding Recipes.—The formulations of the vulcanizates prepared for the purpose of correlation of adsorption and reinforcement are given in Table II. Abrasion tests on the cured stocks were carried out on a Goodyear-Huber laboratory angle abrader, at a wheel angle of 15°.

RATE OF ADSORPTION

There are several reports in the literature to the effect that the adsorption of high polymers from solution is a fairly rapid process, requiring only a few hours for establishment of equilibrium¹¹. An independent rate study showed that this is definitely not true for the adsorption of elastomeric molecules on carbon black from *n*-heptane solution. The adsorption rates were found to depend on the polymer, the specific surface area of the carbon black, and the concentration of the solution. These relationships are illustrated by Figures 1 to 3. The concentrations indicated are the final apparent equilibrium concentrations (in grams per liter). The adsorption rates of the three rubbers were in the order of Butyl > cold GR-S > Hevea. Blacks of large surface area attain adsorption equilibrium more slowly than blacks of lower surface area, and

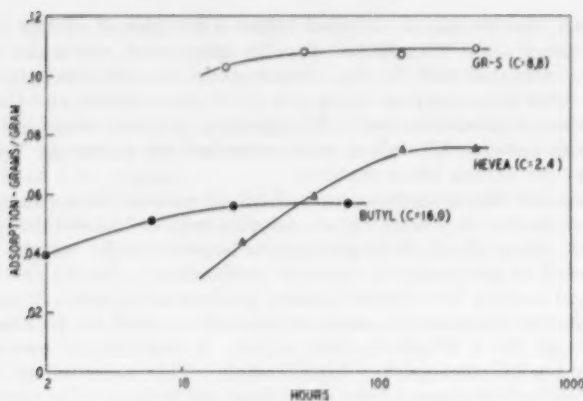


Fig. 1.—Rate of adsorption of elastomers by HAF black.

faster adsorption rates are obtained for the lower concentration points of a given adsorption isotherm. These trends combine to make the determination of an equilibrium isotherm for natural rubber on SAF-type blacks virtually impossible. Even after 2 weeks' adsorption, SAF-Hevea isotherms exhibited abnormally low values relative to their high surface area and, in addition, showed negative slopes at higher concentrations.

It is readily conceivable that the degree of densification of a carbon black might exert an effect on adsorption rate. For this reason adsorption rates on pelleted SAF-I and HAF were compared with those on unpelleted SAF-II and acetylene blacks. The results suggested no significant differences due to pelleting. However, all carbon blacks had been previously extracted in benzene and dried, a treatment which minimizes the differences in bulk density between pelleted and unpelleted samples. For example, the bulk density of SAF-II as charged was only 20 per cent less than that of the SAF-I pellets. Thus, while the results do not rule out a possible effect of densification, it does not appear to be an important factor in the present study.

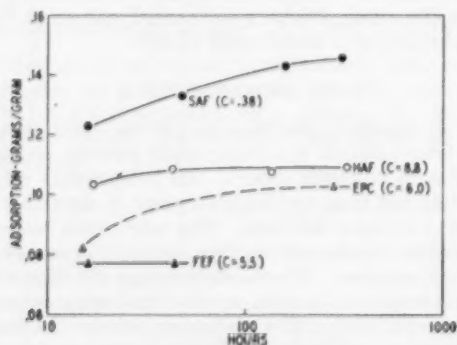


Fig. 2.—Rate of adsorption of 41° F GR-S by various carbon blacks.

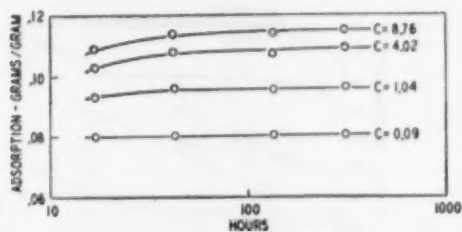


Fig. 3.—Rate of adsorption of GR-S by HAF black as a function of concentration.

On the basis of the rate study, the following adsorption times were chosen for the determination of the equilibrium isotherms:

Rubber	Carbon black	Time (hours)
GR-I-18	All except SAF	18.5
	SAF	88
41° F GR-S	FT, SRF, FEF, acetylene	18
	HAF	44
	Graphon	94
	EPC, SAF	290
Hevea	All except SAF	136

ADSORPTION ISOTHERMS

The apparent equilibrium isotherms are shown in Figures 4 to 6. They resemble Langmuir-type isotherms in that an apparent saturation value is approached, but closer inspection shows them to be much too steep in the dilute solution range; in fact, the initial adsorption is very nearly quantitative. (For the sake of clarity, most of the quantitative adsorption points have been omitted from the figures.) An attempt was made to fit the isotherms to the recently

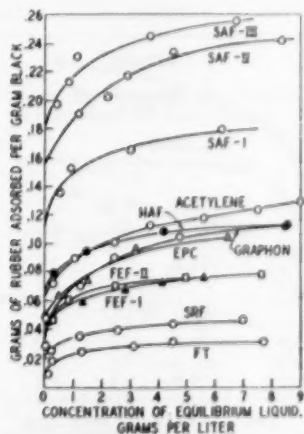


Fig. 4.—Adsorption of 41° F GR-S from n-heptane.

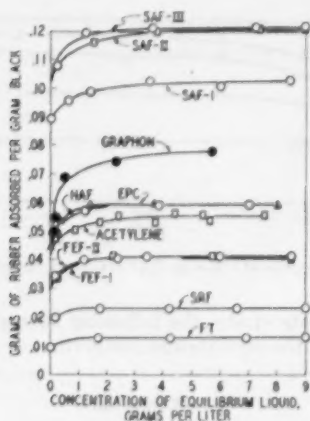


FIG. 5.—Adsorption of GR-1-18 from n-heptane.

developed theory of polymer adsorption of Simha, Frisch, and Eirich⁷. This theory leads to an isotherm of the form:

$$[\theta/(1-\theta)]e^{x_1\theta} = (Kc)^{1/\langle\nu\rangle} \quad (7)$$

where θ is the fraction of the surface covered by polymer segments, $\langle\nu\rangle$ is the average number of segments adsorbed per chain, K is a constant dependent on $\langle\nu\rangle$, the heat of adsorption, solvent interaction, molecular weight, and temperature, and x_1 is a factor expressing the interaction between adsorbed segments in excess over their interaction in bulk. If the excess lateral interactions are neglected ($x_1 = 0$), Equation 7 may be transformed into a form suitable for plotting of experimental data:

$$\log [(a_s/a) - 1] = -\langle\nu\rangle^{-1} \log K - \langle\nu\rangle^{-1} \log c \quad (8)$$

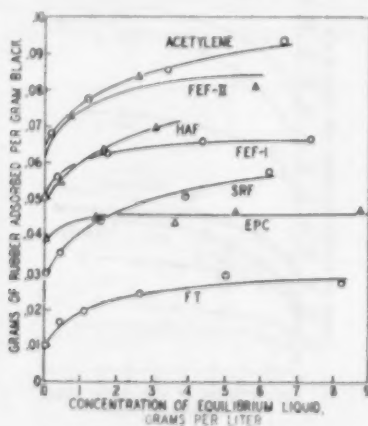


FIG. 6.—Adsorption of No. 1 smoked sheet from n-heptane.

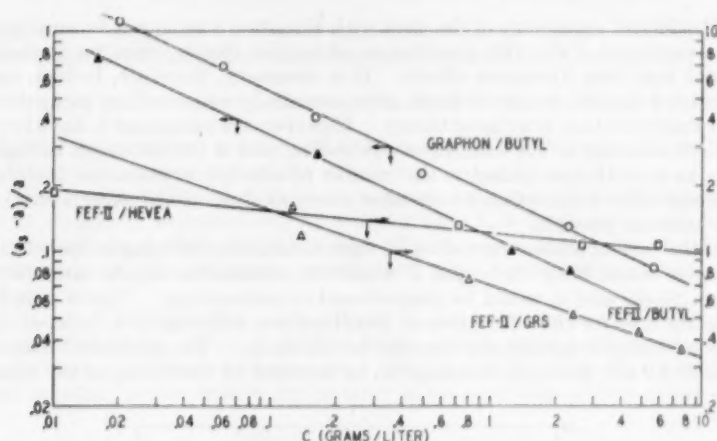


FIG. 7.—Typical test plots of isotherms according to Equation 8.

where a is the adsorption at concentration c , and a_s is its saturation value. One of the features of Equation 7 or 8 is that, when $\langle \nu \rangle$ is appreciably larger than unity, the isotherm appears leveled out long before the adsorption reaches the saturation value, a_s . To fit the experimental data the left-hand side of Equation 8 was plotted against $\log c$ for several assigned values of a_s and the best straight line through the experimental points chosen for the calculation of K and $\langle \nu \rangle$. Figure 7 shows some typical test plots. All isotherms could be fitted to Equation 8 within experimental error; none could be fitted by the Langmuir equation. Unfortunately, however, the isotherms are not very sensitive to the exact choice of the constants K , $\langle \nu \rangle$, and a_s , which is perhaps not surprising in view of the fact that we are dealing with a three-parameter equation. The approximate nature of the constants obtained (Table III) must therefore be borne in mind.

TABLE III
ADSORPTION OF ELASTOMERS ON CARBON BLACK
ACCORDING TO EQUATION 8

Black	41° F GR-S			GR-I-18			Hevea		
	$\langle \nu \rangle$	a_s	K	$\langle \nu \rangle$	a_s	K	$\langle \nu \rangle$	a_s	K
FT	1.70	0.036	3.5	2.2	0.014	107	3.8	0.071	0.024
SRF	2.65	0.067	1.2	2.2	0.0245	155	5.0	0.128	0.03
FEF-I	2.45	0.119	0.8	2.2	0.0435	88	8.0	0.144	0.054
FEF-II	3.10	0.108	3.1	2.2	0.044	109	10.0	0.172	0.07
Acetylene	2.10	0.169	1.2	2.2	0.057	100	7.6	0.192	0.05
EPC	2.40	0.160	0.7	2.2	0.064	100	13.0	0.092	0.09
HAF	3.05	0.155	2.8	2.2	0.062	199	8.0	0.150	0.06
Graphon	1.37	0.140	0.85	2.2	0.0845	40	—	—	—
SAF-I	3.30	0.245	4.2	2.2	0.105	323	—	—	—
SAF-II	2.75	0.328	2.4	2.2	0.125	250	—	—	—
SAF-III	3.30	0.354	4.4	2.2	0.125	393	—	—	—

a_s . Saturation adsorption, grams per gram black.

$\langle \nu \rangle$. Average number of adsorbed segments per polymer molecule.

K . Constant, liters per gram.

The formal agreement of the data with Equation 8 must not be considered a successful test of the SFE equilibrium adsorption theory, since the isotherms are not free from hysteresis effects. It is necessary, therefore, to look upon Equation 8 applied to carbon black as an essentially empirical law incapable of exact interpretation in terms of theory. However, the parameter a_s has obvious physical meaning as the saturation adsorption, and it proves useful to regard $\langle \nu \rangle$ as nevertheless related to the number of adsorption points per molecule. With the latter assumption a somewhat closer analysis of the experimental results becomes possible.

If the carbon blacks were of equal surface activity, differing in specific surface area alone, both $\langle \nu \rangle$ and K would be expected to be the same for all carbon blacks and a_s would be proportional to surface area. This is found to be nearly true for the adsorption of Butyl rubber, although it is believed that $\langle \nu \rangle$ in reality is not strictly constant for all blacks. The deviations from the value of 2.2 are, however, too small to be detected by the fitting of the experi-

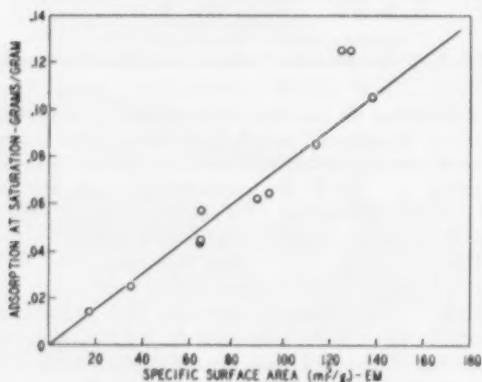


FIG. 8.—Adsorption of Butyl rubber as a function of surface area.

mental data to Equation 8. The correlation of a_s with electron-microscope surface area is satisfactory except for SAF blacks II and III (Figure 8). It is believed that the electron-microscope areas of these carbon blacks are in error, owing to failure of the method to resolve the smallest particles in extremely finely divided solids. This difficulty could be overcome by plotting a_s against BET surface area; such a plot would then show the channel black to be abnormally low in polymer adsorption. It must be recalled, however, that the surface pores of channel black are not accessible to rubber¹², so that the most valid comparison of polymer adsorption is, indeed, with the electron microscope results. In the example of GR-S it is no longer possible to fit the experimental data for all blacks with a single value of $\langle \nu \rangle$. Although the values of a_s are still roughly proportional to surface area, some pronounced exceptions are observed. It is noted, however, that large values of $\langle \nu \rangle$ are frequently associated with values of a_s which are smaller than might be expected on the basis of surface area. This would be reasonable in view of the assumption made regarding the significance of $\langle \nu \rangle$, for any given number of adsorption sites would accommodate more total adsorbed polymer if the molecules were

attached at a smaller number of segments along the chain. The number of adsorption points per unit area of adsorbent at saturation would be simply:

$$n = \langle \nu \rangle a_s N / MS \quad (9)$$

where N is Avogadro's number, M is the molecular weight of the rubber, and S is the specific surface area of the adsorbent.

The results of Figures 4 and 5 also suggest some connection of carbon black chain structure, as exemplified by acetylene black, with elastomer adsorption. Unfortunately, present-day knowledge of the causes underlying structure in carbon blacks is too meager to permit even a qualitative interpretation of this effect.

Some of the anomalies in the natural-rubber isotherms are probably due to degradation of the rubber in solution in the course of the determination of the isotherm and in storage between runs. Reproducibility of the Hevea isotherms was definitely poorer than in the instance of the synthetic rubbers unless dupli-

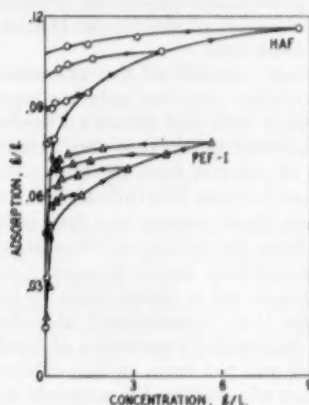


FIG. 9.—Hysteresis of cold rubber adsorption from *n*-heptane.

cate runs were charged simultaneously. It is believed, therefore, that the unusually large difference between the two FEF blacks and the relatively small adsorption of HAF are of doubtful significance.

ADSORPTION HYSTERESIS AND BOUND RUBBER

All adsorption isotherms obtained exhibit strong hysteresis effects. Typical hysteresis loops are shown in Figure 9 for the adsorption of GR-S on FEF and HAF blacks. Graphon exhibits the same behavior. In order to establish the limit of irreversible adsorption, a series of experiments was performed in which the blacks carrying the adsorbed rubber films were transferred directly to Soxhlet extractors and extracted for 72 hours. If *n*-heptane was used as the extraction liquid, the total amount of unextractable polymer agreed closely with the value obtained by extrapolation of the desorption isotherms to zero concentration. If a better solvent, such as benzene, was used as the extraction liquid, more rubber could be desorbed, but the amount of irreversibly adsorbed polymer was still larger than the quantity of polymer that could be adsorbed directly

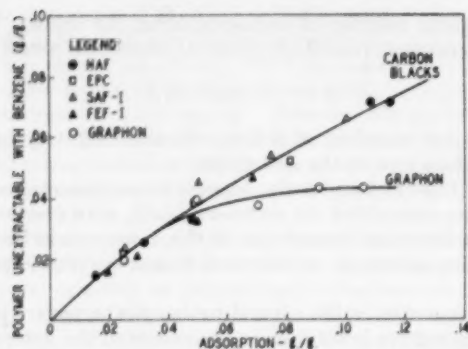


FIG. 10.—Extraction of adsorbed polymer from carbon black. 41° F GR-8.

from benzene solution. These observations are illustrated by Figure 10. The close resemblance of the behavior of the rubber blacks and the distinctive behavior of Graphon are conspicuous.

These results are clearly related to the phenomenon* of bound rubber. Since the amount of irreversibly adsorbed polymer increases with the quantity of polymer adsorbed to start with and shows no tendency to level out in the range observed, it is not difficult to imagine very extensive irreversible adsorption following adsorption of polymer from the bulk phase. Recently Watson¹³ has presented evidence that polymer free radicals are formed in the cold milling of rubber, and that carbon black, acting as a free radical acceptor, combines with these chemically to form the carbon-polymer gel complex. There is considerable evidence to support this, but it is equally obvious from the results presented here that milling is not a prerequisite to bound rubber formation. In his paper Watson states that "dispersions" of carbon black in rubber prepared by freeze-drying a ball-milled suspension of black in a benzene solution (a good solvent) of rubber will not form carbon-rubber gel. However, under these conditions adsorption of considerable amounts of rubber is not likely to

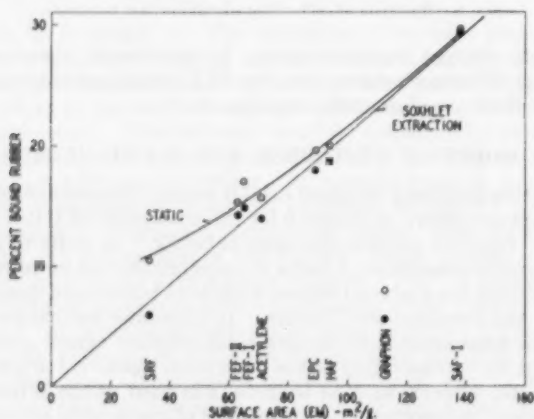


FIG. 11.—Bound rubber at 50 parts per 100 parts of rubber in 41° F GR-8.

occur, and therefore no pronounced bound rubber development should be expected. The process of insolubilization of rubbers by carbon black may well take place in two steps: a rapid physical adsorption of polymer followed by a slower reaction of the adsorbed polymer with the black. This might explain the adsorption hysteresis as well as the high level of bound rubber in mill-mixed stocks.

It is well known that the quantity of bound rubber formed under equal mixing conditions is a function of the (external) surface area of the carbon black. When the bound-rubber determination is carried out by continuous extraction with fresh solvent, the amount of bound rubber is directly proportional to surface area for all carbon blacks except Graphon (Figure 11). Blacks of large particle size which do not form a coherent gel at 50 parts per 100 of rubber nevertheless form bound rubber; the particles are, however, too far removed from each other to permit their fusion into a continuous network by polymer molecules which have become adsorbed on more than one particle. By assuming a complete dispersion, it is possible to calculate a critical filler concentration for the formation of a coherent gel for any carbon black.

Let the volume fraction of carbon black be:

$$v = N\pi d^3/6 \quad (10)$$

where N is the number of particles per cubic centimeter and d is the particle diameter, and let a packing factor, γ , be defined such that:

$$\gamma = Na^3 \quad (11)$$

where a is the mean center to center distance between nearest neighbors in a well-dispersed black-rubber mix. As the filler loading is increased, the surface to surface distance between particles ($a - d$) will eventually become of the order of magnitude of a coiled polymer molecule. At this point a large number of rubber molecules will be irreversibly adsorbed by more than one black particle leading to a coherent carbon gel. If we denote this critical distance as l_c , we have at once:

$$N_c = \gamma/(d + l_c)^3 \quad (12)$$

and

$$v_c = \pi d^3 \gamma / 6(d + l_c)^3 \quad (13)$$

the subscripts c denoting the values of N and γ at the critical loading. In terms of specific surface area this gives:

$$v_c^{-1} = (6/\pi\gamma)^{1/3} \times (1 + S\rho l_c/6) \quad (14)$$

where ρ is the density of the filler particles. In introducing the surface area, d has been implicitly taken as the area average diameter rather than the arithmetic mean diameter. In view of the approximate nature of the calculation and the none too realistic assumption of an ideal dispersion, such fine distinctions are without consequence. Figure 12 represents a test of Equation 14. The two points shown for each black represent the largest loading observed at which the sample dispersed and the smallest loading at which a coherent gel was formed. From the slope of the line drawn, $l_c = 140 \text{ \AA}$ and $\gamma = 0.61$. The distance l_c is of the correct order of magnitude to represent a dimension characteristic of the coiled polymer molecules. The packing factor of 0.61 would correspond very nearly to a coordination of four, i.e., a roughly tetrahedral ar-

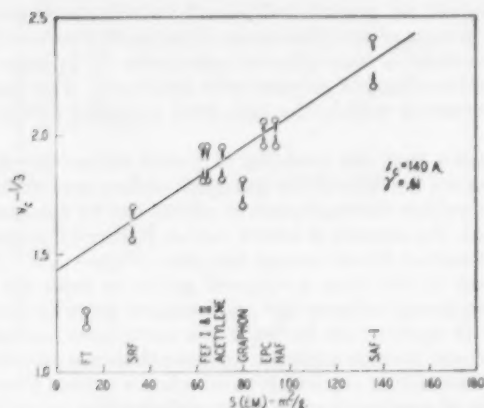


FIG. 12.—Critical loading of black for coherent gel formation in 41° F GR-S.

range of the black particles. Heat treatment which raises the bound-rubber level would undoubtedly shift the curve of Figure 11 in such a way as to make l_c larger. This is to be expected, since the increased number of adsorption points along the polymer chain would allow more of the less frequent, longer molecules to participate in the cross-linking process. Of course, if a free radical mechanism is involved in the formation of bound rubber, then a chain reaction which would also involve formation of new rubber to rubber cross-links is easily envisaged. The effect would likewise be an increase of l_c as the molecular weight is built up.

Because of the simple dependence of bound rubber on surface area in GR-S, the quantity of gel suggests no differences in specific reinforcing potential of the various blacks in this rubber, fine thermal black and Graphon forming the lone exceptions. The abnormally high critical concentrations and low bound-rubber contents of these blacks are indicative of lower activity.

The development of bound rubber on static heat treatment in a neutral (nitrogen) atmosphere follows a strikingly simple pattern in GR-S. Figure 13

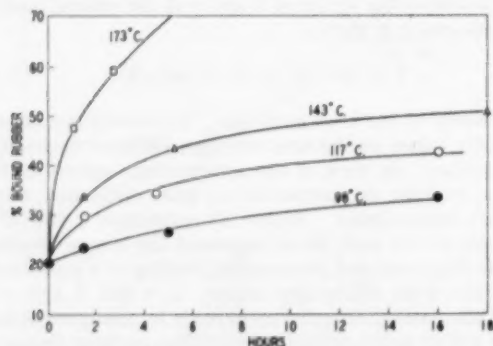


FIG. 13.—Rate of bound rubber formation for HAF-41° F GR-S mix.

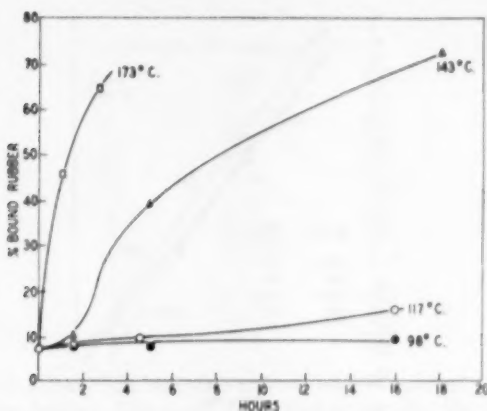


Fig. 14.—Rate of bound rubber formation in Graphon-41° F GR-S mix.

shows the data for HAF black; similar curves have been obtained for FEF, EPC, and SAF carbons. Figure 14 gives the data for Graphon, where the appearance of the curves is quite different. The gelation effect observed at the high temperatures (143° and 173° C) is not derived from adsorption but from cross-linking of the polymer matrix. As Sweitzer and Lyon¹⁴ have shown, carbon black acts as an antioxidant for GR-S. If this action is due to the ability of the black to act as a free radical acceptor, then the behavior of both Graphon and the fully reinforcing blacks can be understood. Graphon with a small number of sites capable of entering into reaction forms little bound rubber, after which its capacity to function as antioxidant is largely spent. Active carbon blacks apparently contain a sufficient number of sites to prevent polymer to polymer cross-linking by forming bound rubber instead. Good evidence for the distinct nature of the carbon black and Graphon gels can be obtained from swelling measurements. In Figure 15 the quantity of bound rubber is

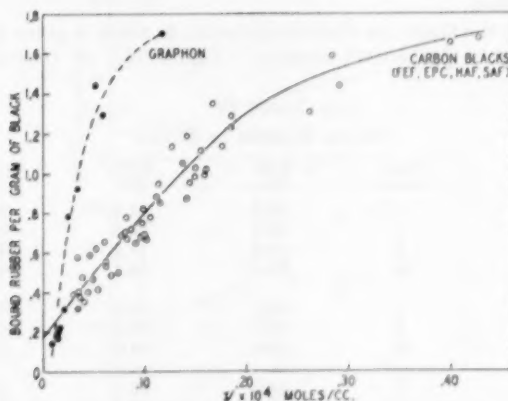


Fig. 15.—Apparent number of network chains in 41° F GR-S carbon gel.

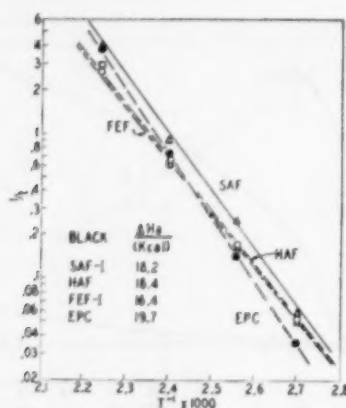


FIG. 16.—Activation energy for bound rubber reaction.

plotted against the apparent number of network chains per unit volume, ν , calculated from the Flory and Rehner¹⁸ theory of swelling:

$$\nu = -\frac{1}{V_s} \times \frac{\ln(1 - v_r) + v_r + \mu v_r^2}{v_r^{1/3} - \frac{v_r}{2}} \quad (15)$$

Here v_r is the volume fraction of polymer in the swollen gel (in this case carbon black excluded), μ is the Huggins solubility parameter, and V_s is the molar volume of the solvent. Essentially a single curve is followed by all blacks except Graphon, suggesting a clear distinction in the two types of gel formed. In either case the volume density of network chains increases as the bound rubber level rises, an indication that not only new chains are added to the network but also the existing network is being further cross-linked or, in the case of bound rubber, the same molecules become attached to the surface over and over again at new sites.

By plotting the times (or their reciprocals) to reach a given bound rubber level according to Arrhenius' equation (Figure 16), an over-all activation

TABLE IV
BOUND RUBBER IN HEVEA

Temp. (°C)	Time (hours)	HAF (%)	EPC (%)	Graphon (%)
98	—	32.5	34.2	26.9
	1	36.3	36.5	28.5
	5	48.0	47.2	35.7
	16	52.4	56.1	40.2
137	1	39.4	45.8	31.8
	5	48.7	59.9	41.0
	16	49.0	64.0	39.5
178	1	44.0	53.1	33.9
	5	45.8	61.4	34.0
	16	44.7	61.7	36.0

TABLE V
BOUND RUBBER IN BUTYL

Temp. (° C)	Time (hours)	HAF (%)	EPC (%)	Graphon (%)
98	—	23.8	37.1	17.9
	1	19.6	28.6	15.3
	5	16.7	35.2	17.2
	16	17.9	43.3	14.7
137	1	13.4	30.5	14.7
	5	20.0	46.0	16.2
	16	24.6	51.8	17.4
178	1	17.3	38.3	15.1
	5	26.7	46.0	16.7
	16	30.6	44.3	12.4

energy for the GR-S-carbon black reaction can be calculated. The results are indicated on the figure. The mean activation energy for the four blacks is 18 kcal., in remarkably good agreement with similar estimates by Barton, Smallwood, and Ganzhorn¹⁶ and Rehner and Gessler¹⁷. It is interesting that Barton, Smallwood, and Ganzhorn obtained their activation energy (for Hevea) from consideration of electrical resistivity changes, while Rehner and Gessler obtained their value in Butyl rubber by considering modulus changes on heat treatment. Attempts to determine the activation energies for Hevea and Butyl by the bound-rubber method were unsuccessful, because it has so far not been possible to exclude side reactions. The data for natural rubber pass through a maximum with time and temperature; in Butyl a minimum is obtained at short heating times, the nature of which is not understood (Tables IV and V).

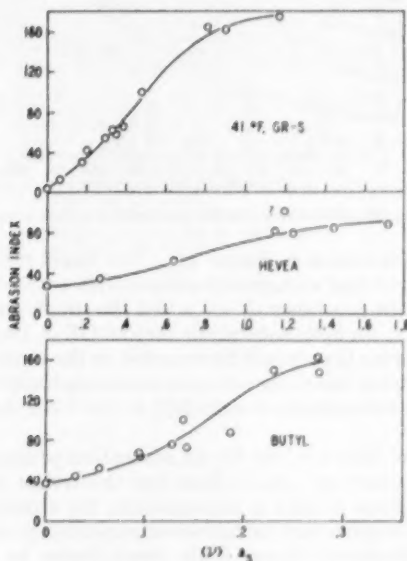


FIG. 17.—Relation of abrasion resistance to adsorption.

ADSORPTION AND REINFORCEMENT

The results of the various desorption experiments suggest that all carbon blacks, with the exception of thermal and graphitized carbons, are really similar in their specific activity toward various rubbers, the distinguishing feature being their particle size or surface area. The adsorption isotherms from solution appear to be somewhat more discriminating. The product of $\langle \nu \rangle$ and a_s may be chosen as representative of the relative over-all activity. If the SFE theory were to apply exactly in the form of Equation 8, this product would in fact be proportional to the number of adsorption sites per unit weight of black under the conditions of the adsorption experiment (compare with Equation 9). Figure 17 shows laboratory abrasion indices plotted against $\langle \nu \rangle a_s$. The correlation is good, particularly in view of the relatively poor sensitivity of the adsorption data toward the exact choice of $\langle \nu \rangle$. A similar plot of abrasion

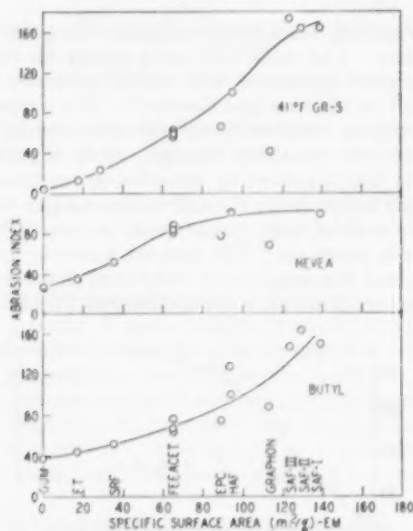


FIG. 18.—Relation of abrasion resistance to surface area.

against surface area is shown in Figure 18. The Butyl rubber data show approximately the same trend with surface area as with adsorption, which is to be expected in view of the constancy of $\langle \nu \rangle$ and the simple surface area dependence of a_s (Figure 8). In both natural rubber and GR-S, Graphon and channel black are less reinforcing than would be expected on the basis of specific surface area alone. On the other hand, the abrasion resistance imparted by these blacks to GR-S and Hevea vulcanizates is definitely in line with their adsorption product, $\langle \nu \rangle a_s$.

The estimation of filler activity by its adsorption product in solution is at best a rough approximation. Aside from the theoretical limitations already discussed and the failure to take K into account, the physical situation which exists in condensed systems such as rubber vulcanizates, or even carbon-rubber masterbatches, undoubtedly bears little resemblance to solution-adsorbed rubber. The results of the bound rubber experiments amply illustrate this

point. The fact remains, however, that, regardless of their origin, the adsorptive forces involved in reinforcement should also exert themselves to some extent in solution. The extensive hysteresis which is observed both in solution and in bulk adsorption suggests that we are dealing with essentially the same phenomenon. The irreversibility of the adsorption indicates that the mechanism cannot be purely physical, although van der Waals adsorption undoubtedly accompanies the chemisorptive process. Furthermore, if one is willing to accept the view that the formation of carbon gel on heating is primarily an adsorption process, its high activation energy would clearly identify it as chemical in nature.

As expected, the conclusions which may be drawn from adsorption and bound-rubber experiments are similar, the consensus being that the majority of carbon blacks do not differ appreciably from each other in their specific adsorption and reinforcing characteristics toward elastomers. As a consequence, the main effect on reinforcement as exemplified by abrasion resistance is simply derived from the state of subdivision, i.e., particle size or surface area. In those instances where the simple surface area dependence of abrasion fails, abnormalities in the adsorption-desorption behavior are observed. These are found mainly in Graphon, and to a lesser extent in channel and thermal blacks.

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THE EFFECT OF OZONE ON NEOPRENE VULCANIZATES AND THE INFLUENCE OF SOME PROTECTIVE AGENTS AND FILLERS *

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INTRODUCTION

In this investigation an attempt was made to show a certain analogy between the nature of the phenomenon of the crystallization of an undercooled melt and ozone crack formation in stretched natural or synthetic rubber, in order in this way perhaps to have some starting point for a more detailed experimental investigation of these interesting problems. At the same time the observed qualitative differences in the effects of ozone on natural rubber vulcanizates and on Neoprene vulcanizates might be explained. In the experimental part it is first shown, with the help of a simplified experimental method, that the rate of crack growth can be considerably reduced by the presence of protective agents. In addition, a great change in the temperature dependence of crack growth is observed under certain conditions. It can not yet be decided whether or not the rate of nuclei formation is similarly influenced. Furthermore, vulcanizates containing different fillers and different Neoprene contents have been examined.

THEORETICAL DISCUSSION AND NATURE OF THE PROBLEM

It is common knowledge that Neoprene vulcanizates show an appreciably better resistance to ozone and weather effects than does natural rubber. Nevertheless, in vulcanized Neoprene mixtures large or small cracks, more or less numerous, running parallel to each other, often appear during service in the open air or in close proximity to strong electric fields. It is safe to assume that the development of these cracks in natural rubber, as also in Neoprene, can be attributed to the presence of ozone¹, the content of which in the atmosphere is only of the order of magnitude of 10^{-8} to 10^{-6} per cent². But even ozone concentrations of this magnitude can prove destructive during long times of exposure. It can be assumed that, in this case, the double bonds in the polymer are attacked by the ozone, yet little is known as yet of the details of the physical-chemical changes which take place and lead to the development of cracks³.

In order to obtain a definite insight into the reactions in question, crack formation in natural-rubber vulcanizates has been examined from different angles in its dependence on external conditions⁴, and it has been proved that the presence of mechanical strains in the rubber material is to be regarded as a prerequisite for the formation of ozone cracks. A deformation of 5 per cent suffices to fulfill this requirement.

* Translated from *Kautschuk und Gummi*, Vol. 8, No. 2, pages WT 35-39, February 1955.

Based on these findings, the opinion has been expressed² that the process of crack development can be divided into two concurrent processes: on the one hand, the formation of local microscopically small "crack nuclei" and, in addition, the growth of these crack nuclei into macroscopically visible cracks.

We are of the opinion that these phenomena are comparable to the crystallization of a fused substance. Just as in this latter case, the number and size of the developing crystals, according to the degree of supercooling, are governed first, by the rate of formation of crystal nuclei and, second, by the rate of growth of the developed nuclei³, we may likewise regard the number and growth of the ozone cracks which develop in a material under a given set of conditions as the result of the combined effect of the rate of formation of these crack nuclei and the rate of crack growth. Just as in a crystallizing melt, the number of nuclei is relatively small, that is, only a few of the molecules present fulfill the neces-

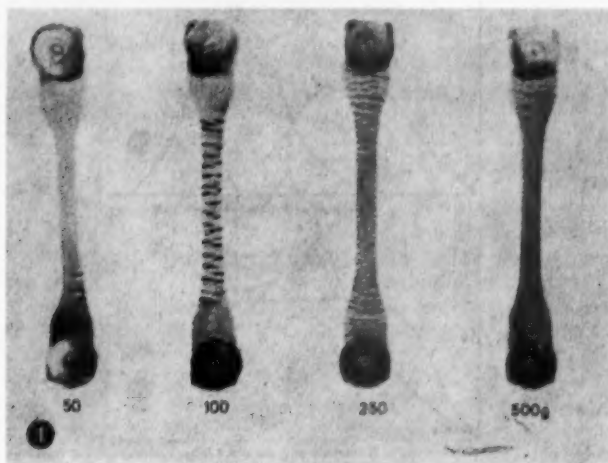


FIG. 1.—Effect of ozone on a natural-rubber vulcanizate loaded with 50, 100, 250, and 500 grams, respectively.

sary conditions for nuclei development, there are, in a rubber product exposed to ozone, only relatively few spots which conform to the conditions necessary for the formation of crack nuclei; for between the tears there are always small, but measurable, interstices, on the surface of which no deformation can be recognized, even microscopically. The localized coincidence of the conditions necessary for nuclei formation is, therefore, controlled by the laws of probability, both in the case of crystallization⁴ and of ozone-crack formation. Smith and Gough⁵ express the following ideas in this respect: "A crack arises at that region only if several double bonds, one in each of the segments in the several molecules, are simultaneously attacked by ozone. The simultaneous breaking by ozone of adjacent stress-carrying molecules (or segments thereof) at the points where these molecules pass through a plane perpendicular to the applied stress results in the movement apart of the free radicals or molecule ends by an amount sufficient to constitute a permanent physical or mechanical discontinuity, and recombination of the free radicals or molecule ends is prevented."

Figure 1 illustrates these conditions. It shows ozone cracks developed in test-specimens of a natural-rubber vulcanizate with different loads, but otherwise under identical conditions. It is obvious that, with slight stretching (50-gram load), the rate of development of crack nuclei is very slow, but increases sharply with increased tension.

The speed of crack development, however, and the crack extension after a certain time, decreases with increasing load. Because of the coincidence of these two factors, there is evidently a medium loading where ozone cracks of maximum extension develop within a definite period, an observation made from another source and discussed as the concept⁷ of "critical elongation".

In our opinion, this phenomenon can be considered analogous to the development of maximum crystals (within a definite time span) from a crystallizing melt. Crystals of maximum size will result within the considered time

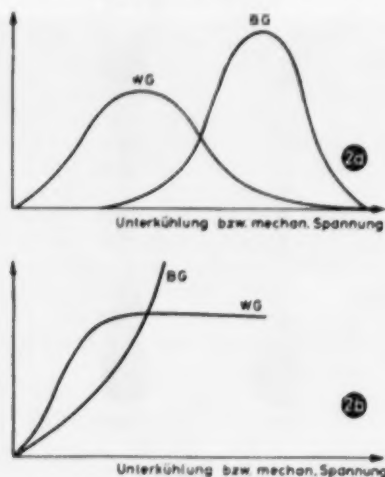


FIG. 2.—Rate of growth of crack nuclei (WG) and rate of formation of crack nuclei (BG) in relation to the undercooling or mechanical stress. The abscissa indicates the undercooling or mechanical stress.

span if the rate of crystal growth (WG) and the rate of nuclei formation (BG) in relation to supercooling follow the course shown schematically⁸ in Figure 2a, and the melt crystallizes in a temperature interval between the two curve maxima, where the rate of nuclei formation, which increases with increasing supercooling, has already attained a sufficient rate and the sharply decreasing growth rate is still large enough. On the other hand, with less supercooling, the probability of the formation of crystal nuclei within a limited time span is too small on account of the low rate of nuclei formation; with stronger supercooling, however, numerous crystals of small size occur. Because of this analogy, the conclusion seems obvious that the dependence of the rate of crack growth and the rate of crack nuclei formation on mechanical stress in the case of natural rubber can be assumed to be similar to the relations in Figure 2a.

Conditions seem to be somewhat different in the case of ozone crack formation of Neoprene vulcanizates. Here too, mechanical strains in the material are necessary for the formation of ozone cracks, but a critical tension has never been actually observed⁹.

Figure 3 gives, as an example, the formation of ozone cracks in a Neoprene vulcanizate under different loadings (testing time and ozone concentration were several times larger than in Figure 1). It can easily be seen that in this case the number, as well as the extension of the cracks increases uniformly with the loading. When loaded with 700 to 1000 grams, the samples were badly cracked even before the expiration of the testing time. This is in contrast to the conditions described for natural rubber. The rate of crack nuclei formation and of crack growth are not only considerably smaller with respect to their absolute size than in the case of natural rubber, but these values are also displaced with respect to each other in their dependence on mechanical stress in contrast to the representation in illustration 2a, perhaps in the same way⁵ as suggested in Figure 2b.

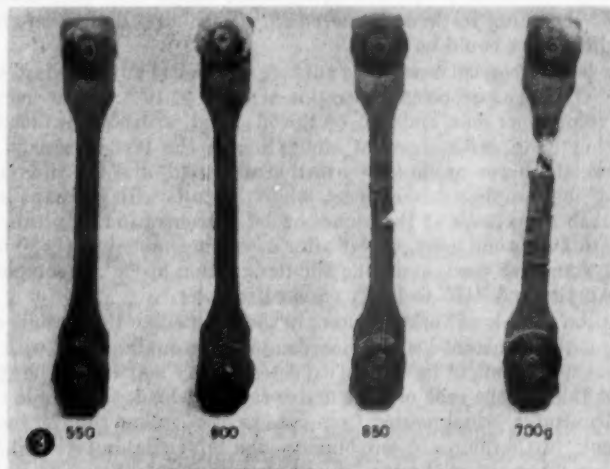


Fig. 3.—Effect of ozone on a Neoprene vulcanizate loaded with 550, 600, 650, and 700 grams, respectively.

This not only quantitative, but also qualitative, difference in ozone crack formation between Neoprene and natural rubber seems to us not unimportant, but we would prefer to wait for a more extensive study of the dependence of the rate of both crack nuclei formation and crack growth on mechanical stress, e.g., at different temperatures and ozone concentrations, to give a fuller explanation of the processes taking place here.

But since such an investigation would necessarily have a rather large scope, and consequently would demand a great expenditure of time, we have first of all carried out survey tests according to a very much simpler method for the purpose of obtaining in this way an idea of the extent of the temperature function of crack formation, especially in the presence of different protective agents.

PREVIOUS INVESTIGATIONS

In recent times, the ozone resistance of Neoprene mixtures was investigated by Thompson, Baker, and Brownlow⁶, who primarily determined the effect of

softeners, protective agents, and accelerators, as well as the degree of loading with various fillers. They obtained the following important results.

1. Softeners with a petroleum base decrease the ozone resistance of Neoprene mixtures almost inappreciably.

2. Ester softeners decrease the ozone resistance to a measurable extent.

3. The type and proportion of the accelerators do not affect the ozone resistance at all at elongations up to 100 per cent.

4. The ozone resistance of mixtures decreases with increasing loadings of filler.

5. Carbon blacks used as fillers impart very much higher ozone resistance to Neoprene mixtures than do calcium carbonate, barytes, and calcium silicate. Kaolin, in this respect, is close in its effect to that of carbon blacks.

6. Twenty different protective agents were tested and were divided into five groups according to their effectiveness. Within each of these groups, no essential differences could be found.

The tests were carried out by the authors mentioned at a standard temperature of 24° C, with an ozone concentration of 1 to 3×10^{-4} volume-per cent and 1×10^{-2} volume-per cent, and also, on the one hand, with constant loading and, on the other hand, with constant elongation of the test materials. In the former case, the lower ozone concentration was used, and the time up to the cracking of the sample was measured, while the tests with constant load were carried out in most cases at the higher ozone concentration. In this case, for the evaluation of ozone tears, visible after a certain time interval (30 minutes), a rating system was used, assigning the designation of "0" to completely unaffected samples and "10" to badly cracked samples.

Thompson and his coworkers found, in the work cited, that results obtained by testing with a constant load do not always agree qualitatively with those at constant tension, as might have been expected. This may in part be attributed to the fact that, in the case of tests under constant load, the tensile strengths of the vulcanizates, which varied from case to case, influenced the results to a great extent; furthermore, in our opinion, the unavoidable personal factor of the observer when using the rating system mentioned above, as well as the generally insufficient differentiation in the evaluation of crack formation, all contribute to the fact that the investigations actually do yield the qualitative results already mentioned, but do not permit a more precise quantitative evaluation.

We have, therefore, tried to reach a quantitative concept from similar investigations carried out on Neoprene vulcanizates under different conditions by utilizing the tensile strength at break of the material before and after the ozone effect as a criterion for the resulting crack formation. Because of the uniform development of crack extension with loading in the case of Neoprene, we consider this method to be a practical one for the survey testing of Neoprene mixtures. The percentage decrease of tear resistance was regarded as a measure of the ozone effect; it depends first of all on the extension of the ozone cracks, that is, the rate of crack growth, and is only slightly influenced by the number of cracks. It is evident that the numerical values obtained by this method¹⁰, which has been used in earlier investigations, may show considerable variations, since in every case the weakest spot in the material will be the starting point of a break. For this reason, we generally averaged four measurements to one mean value. Experience has shown that, in this way, relatively easily reproducible values can be obtained.

EXPERIMENTAL PROCEDURE

The tests were carried out in an apparatus similar to the one used in ASTM D470-49T for testing the ozone resistance of natural rubber (Figure 4).

A current of dried air is passed through an ozonizer and then, after passing through a tempering coil, is led into the ozone chamber in which the samples which are to be tested hang. These test-pieces, dried out in the form of a dumb-bell, are wound around a glass mandrel, the thickness of which (5 mm. diameter) is so measured that the uppermost layer of the 2 mm. thick sample is stretched 25 to 30 per cent. The action of the ozone occurs, therefore, under constant and equal stress for all the test-pieces.

Before and during the tests, it is possible to determine the amount of ozone present in the air current by using a gas burette and allowing a known quantity of ozonized air to flow through the gas washing bottle, in which a previously placed potassium iodide solution absorbs the ozone present, with liberation of

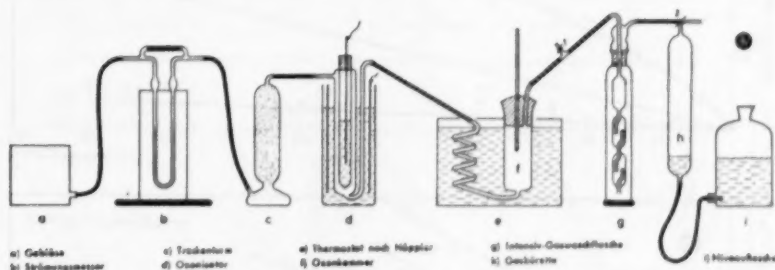


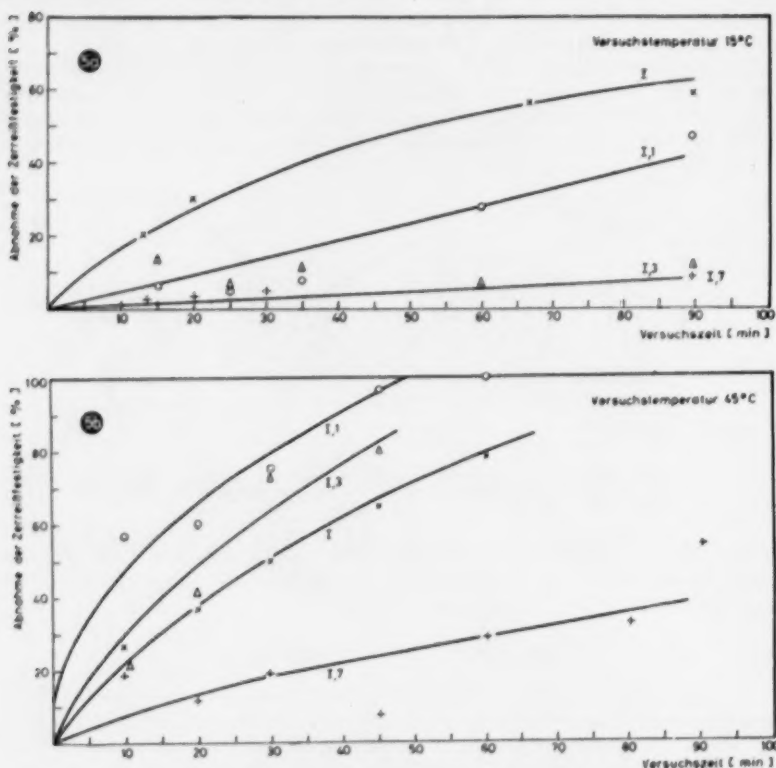
FIG. 4.—Apparatus for testing the ozone resistance of Neoprene. (a) blower; (b) flow meter; (c) drying tower; (d) ozonizer; (e) Höppler thermostat; (f) ozone chamber; (g) intensive gas-washing tower; (h) gas burette; (i) levelling bottle.

iodine. The amount of iodine is determined by titration, and from this the ozone content of the air is calculated. In all tests the ozone concentration amounted to 2.5×10^{-2} volume-per cent.

DISCUSSION OF THE RESULTS

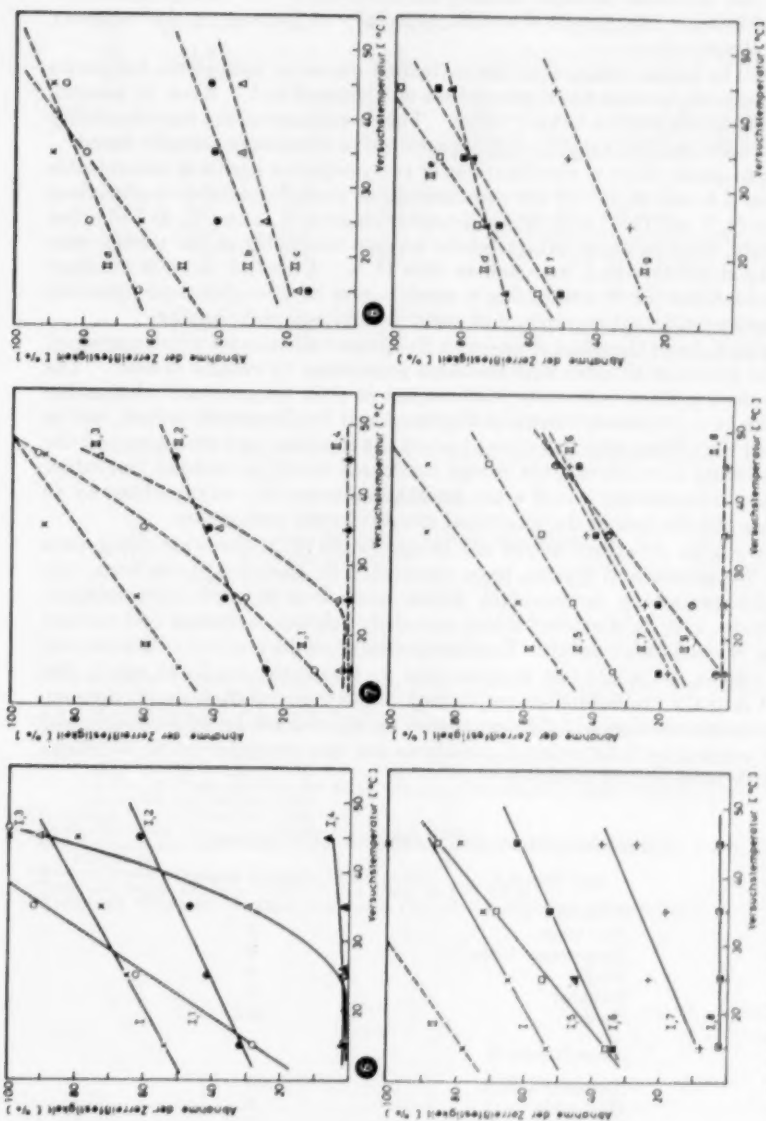
In Figures 5a and 5b, the increase of crack extension is presented, with several examples (as reflected by the decrease of tensile strength) with the time of testing. It should be noted, that the size of the crack increases steadily with the duration of time of exposure to ozone. The bend of the curves is probably due in part to the fact that the samples, bent around the mandrel, have a chance to become partially released from stress because of the formation of cracks. The curves extend to the coordinate zero point; in fact, even when the vulcanizates contain a protective agent (for the composition of the mixtures, see the tables). This points to the fact that, in these cases, an ozone effect takes place from the very beginning of the test, while the slower rise of these particular curves indicates that the growth rate is more or less strongly decreased by these compounds. Whether or not there is an additional influence of the rate of nuclei formation, and whether perhaps some protective agents give protection only for a definite period during a test and after this period permit the ozone effect to take place at normal speed, are questions which must remain unanswered.

A comparison of Figures 5a and 5b shows further that a 30° C rise of the testing temperature of the vulcanizates results in markedly different increases of the ozone effect, e.g., the mixture I,3 containing phenyl-2-naphthylamine as the protective agent shows hardly any visible crack formation at 15° C and is, therefore, in comparison with the base mixture I, effectively protected against ozone, while at 45° C, the same mixture is destroyed at least as completely as the base mixture I at this temperature.



Figs. 5a and 5b.—Increase of crack growth (decrease of tensile strength) of Neoprene vulcanizates from the action of ozone in relation to the time of exposure at 15° C and at 45° C. The abscissas indicate the time of exposure in minutes; the ordinate the percentage decrease of tensile strength.

Figures 6 and 7 represent the action of ozone on the base mixtures I and II containing various protective agents in relation to the testing temperature. Series I was kept in the ozone chamber for 60 minutes, while with series II the test was ended after 30 minutes, because this mixture contained less Neoprene, and consequently the ozone attack was more destructive in this case. The greatly differing effects of the individual additives, as well as the susceptibility to temperature, are obvious. In the latter respect, outstanding examples are phenyl-2-naphthylamine, as well as a hydrocarbon mixture of unknown composition in mixture I. We might regard this, at least in the case of phenyl-2-



FIGS. 6 and 7.—Decrease of tensile strength of Neoprene vulcanizates of the base mixtures I and II containing different protective agents in relation to the temperature after 60 and 30 minutes' exposure to ozone. The abscissas indicate the temperature during exposure; the ordinates the percentage decrease of tensile strength.

FIG. 8.—Decrease of tensile strength of Neoprene vulcanizates of the base mixture II containing different fillers in relation to the temperature after 30 minutes' exposure to ozone. The abscissas indicate the temperature during exposure; the ordinate the percentage decrease of tensile strength.

naphthylamine, as an indication of the mode of action of the compound, in which case we must perhaps imagine an influence of the energy conditions which determine the growth of cracks, especially an increase of the necessary energy of activation.

It will be further noted that the individual curves of each of the two series of vulcanizates, as seen by a comparison of Figures 6 and 7, have, in general, similar positions relative to each other. This is evidence of the reproducibility of the results and the validity of the quantitative differences actually found.

A synergistic effect of combinations of two protective agents is recognizable in curves I, 8 and II, 8. If the combination of phenylcyclohexyl-*p*-phenylene diamine (I, 7 and II, 7) and phenyl-2-naphthylamine (I, 3 and II, 3) had acted additively, then an ozone attack would become noticeable at the testing temperature of 45° C with I, 8 as well as with II, 8. A similar result is obtained with vulcanizate II, 9, containing a combination of phenyl-2-naphthylamine (I, 5) and a condensation product of acetaldol and α -naphthylamine.

Figure 8 shows the effect of ozone on Neoprene vulcanizates which contained different fillers, in all cases with the same percentage by volume of filler. The curves show greater uniformity with respect to their temperature relationship than the ones previously shown in Figures 6 and 7. It should, indeed, not be assumed that fillers take any direct part in the reaction between ozone and the double bonds, in which case the energy conditions would be changed, but rather that they influence the rate of crack growth in a secondary way, perhaps by an irregular distribution of the mechanical stresses in the vulcanizate.

The results described above are in agreement with the weathering tests which Thompson and Catton have reported. In these long-term tests, vulcanizates containing carbon-black fillers, proved to be especially resistant, while those with light-colored fillers, especially calcium carbonate and calcium silicate, reacted unfavorably. Kaolin occupies a middle position in this respect.

In closing, we would like to stress that we regard the results as only a first insight into the undoubtedly complicated conditions and that, in our opinion, more extensive evidence of the dependence of rate of crack nuclei formation and rate of crack growth on external conditions can be expected from an investigation with more refined methods.

COMPOSITIONS OF THE NEOPRENE VULCANIZATES

Base Mixture I	Parts by weight
Neoprene GN-A	100
Zinc oxide	5
Magnesium oxide	2
NA-22	5
Struktol	5
Kaolin	54.3
Base Mixture II	
Neoprene GN-A	100
Zinc oxide	5
Magnesium oxide	2
NA-22	0.5
Struktol	12.5
Kaolin	132

All mixtures were vulcanized for 20 minutes at 143° C.

VULCANIZATES CONTAINING DIFFERENT PROTECTIVE AGENTS

Base Mixture I		Base Mixture II		Substances tested Hydrocarbon fraction of unknown composition (m. 53° C)
No.	(% by wt.)	No.	(% by wt.)	
I,3	1.8	II,2	1.2	1-C ₁₀ H ₇ N:CHCH ₂ CH(OH)CH ₃
I,3	1.8	II,3	1.2	Phenyl-2-naphthylamine
I,4	1.8	II,4	1.2	Commercial mixture of phenyl-1-naphthylamine, di- <i>p</i> -methoxy-diphenylamine and diphenyl- <i>p</i> -phenylenediamine, in proportions of 2:1:1
I,5	1.8	II,5	1.2	Phenyl-1-naphthylamine
I,6	1.8	II,6	1.2	Mercaptobenzimidazole
I,7	1.8	II,7	1.2	Phenylcyclohexyl- <i>p</i> -phenylene-diamine
I,8	3.6	II,8	2.4	Mixture of phenylcyclohexyl- <i>p</i> -phenylenediamine and phenyl-2-naphthylamine in the proportion of 1:1
—	—	II,9	1.2	Mixture of 1-C ₁₀ H ₇ N:CHCH ₂ CH(OH)CH ₃ and phenyl-2-naphthylamine in the proportion of 1:1

VULCANIZATES CONTAINING DIFFERENT FILLERS

Designation	Parts in place of 132 parts by weight of kaolin in Base Mixture II	
IIa	Talc	132
IIb	Active kaolin-like mineral filler	132
IIc	Anacarbon black	90
IId	German gas black (particle size 330Å)	90
IIe	Calcium carbonate	132
IIf	Barytes + 65 parts by weight of kaolin	80
IIg	Electric-arc carbon black	90

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INHIBITION OF RUBBER OXIDATION BY CARBON BLACK *

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Previous publications from this laboratory¹ have reported the pronounced inhibitory action of small amounts of carbon black on the autocatalytic stage of the oxidation of unvulcanized natural and cold rubber. Although all carbon blacks tested have exhibited this behavior, the effect was most marked for those carbon blacks with a substantial amount of chemisorbed oxygen on their surface. Carbon black has been shown to inhibit oxidation during static heating in air and during Banbury mastication². In the former, oxidation inhibition may be determined directly by measuring the effect of carbon black on the oxygen uptake of the sample, but in Banbury mastication this inhibition effect must be estimated indirectly from those properties influenced by scission and cross-linking changes in the polymer. In the previous papers¹ these measurements were confined to percentage of gel and intrinsic viscosity of the polymer. To provide a more comprehensive picture of this inhibitory action of carbon black during Banbury mastication, this report presents the results of various physical tests made on fully compounded and vulcanized stocks prepared from these masticated rubbers. Four polymers were included in the present study—natural rubber, low-temperature GR-S, oil-extended GR-S and Butyl rubber. In all cases, the inhibitory action of carbon black was compared to that of a standard antioxidant.

EXPERIMENTAL

Prior to compounding, each polymer was masticated in a midget Banbury, at specified times and temperatures, under the following conditions.

1. Mastication without additive.
2. Mastication with 2 and 5 parts carbon black.
3. Mastication with 1.5 parts of a chemical antioxidant.

With each polymer, a nonmasticated control was included. To ensure maximum oxidation inhibition with carbon black, an oxidized channel black (Micro-nex W-6) was used which contained approximately 10 per cent chemisorbed oxygen. In several instances a standard HAF black (Statex R) was used for comparison. The chemical antioxidant employed was BLE, a ketone-amine reaction product.

After these initial mastication steps, the stocks were rested for 24 hours and tested for Mooney viscosity and gel content. The latter test was carried out by the method used in these laboratories, employing a modification of the Baker cell. The remaining stock was then compounded in standard fashion, using the

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TABLE I
TEST COMPOUNDS
Hevea cured at 290° F

Smoked sheet	100
Carbon black	50
Zinc oxide	5.0
Stearic acid	2.0
Pine tar	1.5
<i>N</i> -cyclohexyl-2-benzothiazole sulfenamide	0.7
Sulfur	3.0
Low-temperature polymer cured at 290° F	
GR-S X723	100
Carbon black	50
Zinc oxide	3.0
Stearic acid	2.0
Paraflux	4.0
Circosol 2XH	4.0
<i>N</i> -cyclohexyl-2-benzothiazole sulfenamide	1.125
Sulfur	2.0
Oil-extended rubber cured at 290° F	
GR-S-1710	137.5
Carbon black	68.75
Zinc oxide	3.0
Stearic acid	2.0
<i>N</i> -cyclohexyl-2-benzothiazole sulfenamide	1.25
Sulfur	2.0
Butyl cured at 307° F	
GR-I-18	100
Carbon black	50
Zinc oxide	5.0
Stearic acid	0.5
Tetramethylthiuram disulfide	1.0
Benzothiazolyl disulfide	1.0
Sulfur	2.0

recipes shown in Table I. The final carbon loading was brought to the desired level, generally 50 parts per 100 parts of rubber, by the addition of HAF black. The percentage of carbon gel in the finished stocks was then determined. Physical testing of the cured vulcanizates was carried out by the usual methods.

NATURAL RUBBER

Banbury mastication prior to compounding was carried out for 30 minutes at temperatures of 300° and 370° F, which are in the range where antioxidants have been observed to inhibit Hevea breakdown². The results for the lower temperature study, which show the effects of adding 5 parts of carbon black during the mastication stage on the raw and vulcanizate properties of Hevea, are presented in Figure 1. It is evident that, under these low-temperature masticating conditions, carbon black moderated somewhat the drastic drop in Mooney viscosity induced by the Banbury mastication; 2 parts of carbon black and 1.5 parts of BLE showed lesser effect.

The drop in Mooney viscosity during mastication of gum rubber has been related to decrease in molecular weight by Stern⁴ using the empirical equation:

$$10^{-5}M = 0.0623(V_s + 18.7)$$

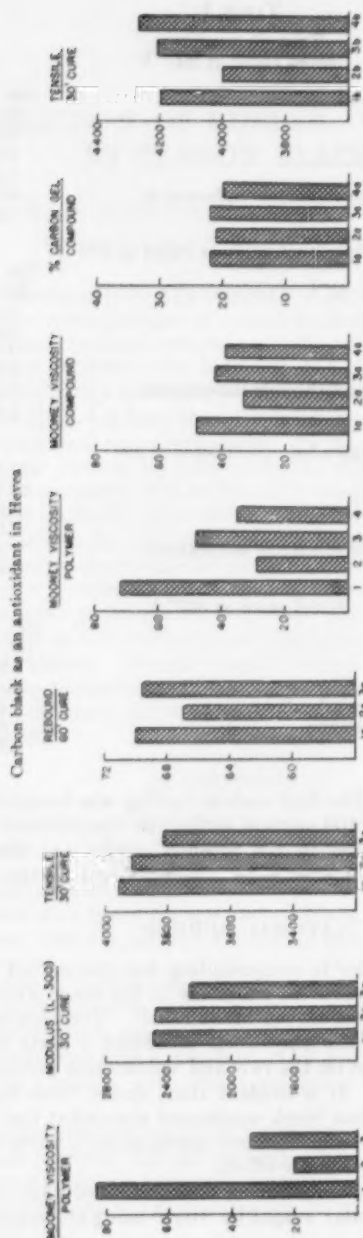


Fig. 1.

- 1 ■ Unvulcanized polymer.
 2. ■ Vulcanized 30 min. at 300° F.
 3. ■ Vulcanized 30 min. at 300° F. with 5 parts oxidized EPC black.
 1a, 2a, 3a. Compounded vulcanizates from 1, 2, 3.

Fig. 2.

1. Unvulcanized polymer.
 2. ■ Vulcanized 30 min. at 370° F.
 3. ■ Vulcanized 30 min. at 370° F. with 5 parts oxidized EPC black.
 4. ■ Vulcanized 30 min. at 370° F. with 1.5 parts BLE.
 1b, 2b, 3b, 4b. Compounded vulcanizates from 1, 2, 3, 4.

where M = molecular weight and V_s = Mooney viscosity. According to this equation, the mastication step in the pure-gum sample lowered the molecular weight from 634,000 to 238,000. Before the calculation of the action of carbon black on molecular weight can be made, the direct effect of the carbon black on the viscosity of the mix must be determined. This may be calculated with a fair degree of accuracy from the Guth-Gold equation⁵.

$$N^* = N(1 + 2.5c + 14.1c^2 + \dots)$$

where N^* = loaded Mooney viscosity; N = gum Mooney viscosity; and c = carbon black concentration.

According to this equation, the direct effect of a 2-part loading of carbon black would be to raise Mooney viscosity by 3 per cent and of a 5-part loading by 9 per cent. Since the observed increases were 23 and 42 per cent, respectively, it is evident that carbon black did suppress the molecular breakdown of the natural rubber to some extent. The action of 1.5 parts of BLE was approximately equivalent to that of the carbon black. This action, however, was not reflected in vulcanizate properties, with the possible exception of resilience. Modulus and tensile strength were, if anything, slightly lower for the stocks masticated in the presence of carbon black and BLE than for the pure gum, although resilience was slightly increased.

The results for Hevea masticated at 370° F, given in Figure 2, offer a partial explanation of these findings. For this mastication temperature, Mooney viscosity for both the uncompounded and compounded stocks was determined. It is evident that carbon black suppressed polymer breakdown to a somewhat greater extent during the 370° F mastication than during the 300° F mastication; the effect of BLE was unchanged. The further mastication with 50 parts of carbon black per 100 parts of rubber involved in compounding then lowered the Mooney viscosity of the control stock considerably, while those of the masticated stocks were relatively unaffected. As a result, the action of the additives is somewhat obscured in the final vulcanizates. The percentage of carbon gel also reflects this situation. Although the 370° F series was also compounded to 40 parts of carbon black per 100 parts of rubber in the expectation of emphasizing tensile differences, only a very slight increase in tensile strength resulted from the presence of carbon black or BLE in the mastication step.

In summary, while the oxidative breakdown of natural rubber during Banbury mastication is inhibited somewhat by the presence of carbon black, the effect is not reflected to any substantial degree in the final vulcanizate properties.

LOW TEMPERATURE GR-S

Mastication was carried out for various times at 225° and 300° F, where in Banbury mastication scission predominates in this polymer, and at 370° F, where gelation is the reaction dominating the final properties of the low temperature polymer⁶ (LTP).

The 225° F results, which were similar to those obtained at 300° F, are presented in Figure 3. They show the typical high resistance to breakdown of cold rubber; Mooney viscosity of the uncompounded stock decreased only slightly. The presence of carbon black, but not of BLE, tended to modify the extent of the viscosity reduction but, as in the natural rubber, the further mastication involved in final compounding minimized the effect of carbon black on compounded Mooney viscosity. Modulus was unaffected, and tensile

strength, as shown in the graph, was only slightly lowered the additives having no effect.

In contrast to the low temperature results, carbon black produced drastic changes in the physical properties of vulcanizates compounded from the rubber masticated at 370° F. The effect of oxidized EPC and standard HAF black on Mooney viscosity and gel development, when present during the mastication stage, is compared to that of BLE in Figure 4. The hot mastication step left Mooney viscosity of the gum stock practically unchanged and raised the compounded Mooney only slightly. This result is to be expected, since gelation, which tends to raise the viscosity, and scission, which tends to lower it, are occurring simultaneously. It has been observed that gel content of less than about 40 per cent lowers Mooney viscosity, while a percentage greater than 50 generally raises it. The presence of the oxidation inhibitors tends to leave the viscosity at its original level by suppressing both scission and gelation.

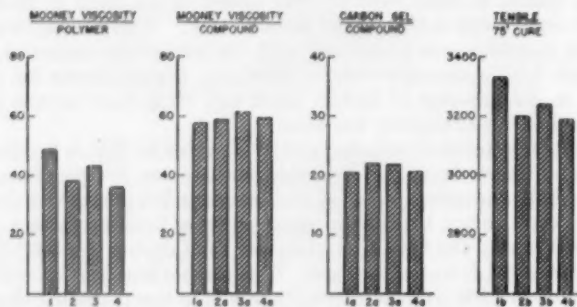


Fig. 3.—Carbon black as an antioxidant during 225° F mastication of low temperature polymer.

1. Unmasticated.
2. Masticated 40 min.
3. Masticated 40 min., with 5 parts oxidized EPC black.
4. Masticated 40 min., with 1.5 parts BLE.
- 1a, 2a, 3a, 4a. Compounded stocks from 1, 2, 3, 4.
- 1b, 2b, 3b, 4b. Compounded vulcanizate from 1a, 2a, 3a, 4a.

Although all additives were effective in suppressing gel formation 5 parts of oxidized EPC per 100 parts of rubber was again more active than HAF black, with both carbons superior to BLE. The same relative positions were maintained in the finished stock. Compounding left the benzene-insoluble portion of the rubber practically unchanged, i.e., 42 per cent in the gum and 40 per cent in the compounded material. Apparently the shearing action of the carbon black in disintegrating polymer gel balanced its adsorptive action in forming carbon gel.

Cold rubber has been found to be quite variable in its tendency to form gel during hot mastication. The polymer used in previous work² required a mastication time of 30 minutes at a temperature of at least 375° F to form a measurable quantity of gelled rubber. With the LTP used in the work described here, measurable amounts of gel formed within 10 minutes at 370° F. Even using the same bale of cold rubber, some difficulty was experienced in obtaining reproducible results. Another indication of the greater gelation activity of the cold rubber used in this study was the carbon loading required to produce maximum inhibition of gel formation. In previous tests this optimum loading

Carbon black as an antioxidant in low-temperature polymer

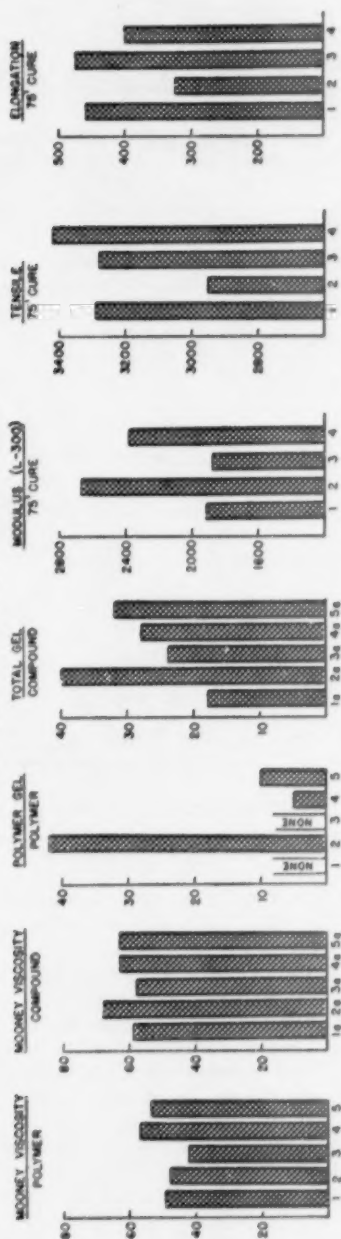


FIG. 4.—Unvulcanized stocks.

FIG. 6.—Vulcanized stocks.

1. Unmasticated polymer.
 2. Masticated 20 min. at 370° F., with 5 parts oxidized EPC black.
 3. Masticated 20 min. at 370° F., with 5 parts HFF black.
 4. Masticated 20 min. at 370° F., with 1.5 parts HFF.
 5. Masticated 20 min. at 370° F., with 1.5 parts BLE.
- 1a, 2a, 3a, 4a, 5a. Compounded stocks from 1, 2, 3, 4, 5.

was approximately 2 parts of oxidized EPC black per 100 parts of rubber but in the reported tests, as revealed in Figure 5, 5 parts per 100 parts of rubber were necessary for maximum gel inhibition. Apparently a 2-part carbon black loading does not provide enough surface for maximum inhibition with the more easily gelled cold rubber used in this study.

Hunter and coworkers⁷, however, found 300° F mastication on an open mill for 30 minutes to produce over 60 per cent gel in GR-S-1503. The different polymerization formulas of GR-S-1503 and -1500 types and the greater availability of oxygen in mill mastication are the probable causes of the easy gelation observed with GR-S-1503.

The inhibition of gel formation during the hot mastication step produced significant changes in the physical properties of the stocks compounded from the masticated polymer. As shown in Figure 6, the presence of carbon black

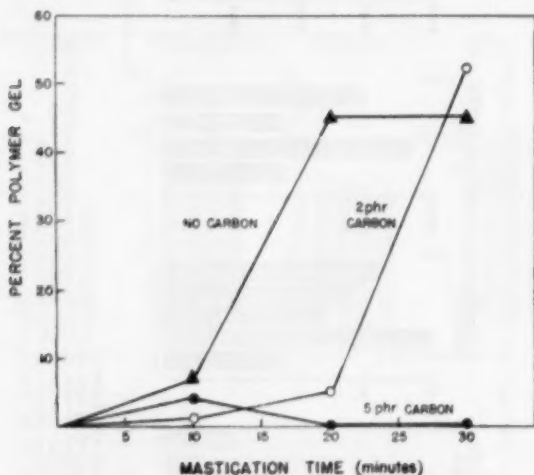


FIG. 5.—Effect of oxidized EPC black dosage on gelation of low-temperature polymer during 370° F mastication.

during the hot mastication step lowered modulus but raised the tensile strength and elongation of the vulcanized stocks. White and coworkers⁸ observed generally similar effects on the physical properties of standard GR-S when this polymer was masticated alone and in the presence of 50 parts of EPC black per 100 parts of rubber. They suggested that the increased modulus and decreased tensile strength of GR-S containing a high proportion of gelled rubber resulted primarily from the inability of the reinforcing pigment to enter the gelled units. Hence, dispersion of the carbon in the polymer is nonuniform with a 100-part carbon loading in the sol portion and zero carbon in the gelled portion, assuming a 50 per cent gel. The finding in this investigation that scission of the polymer chains in natural and cold rubber during 300° F mastication produces relatively little effect on vulcanized physical properties compared to the effects due to gelation confirms the suggestion that gelation and not scission is the predominant factor altering the physical properties of the vulcanized stocks.

In summary, small amounts of carbon black present during 300° F mastication have little effect on the vulcanizate properties of cold rubber, but produce

Carbon black as an antioxidant in oil-extended polymer

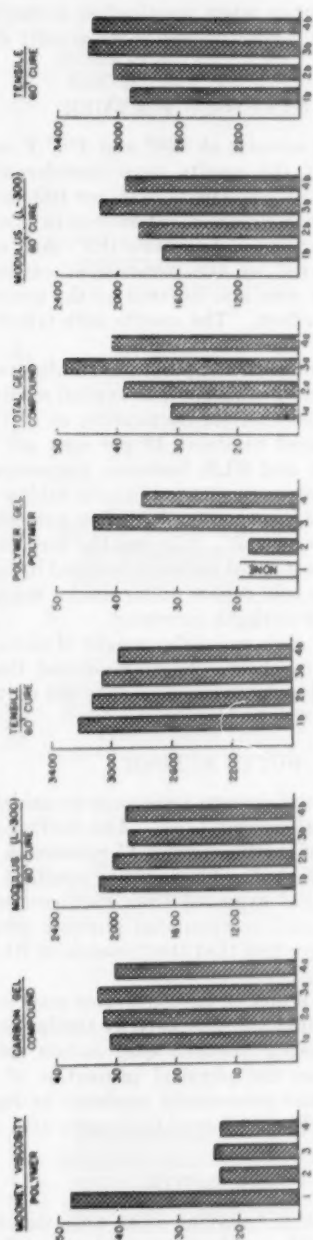


Fig. 7.

1. Unmasticated polymer.
2. Masticated 30 min. at 300° F.
3. Masticated 30 min. at 300° F. with 5 parts oxidized EPC black.
4. Masticated 30 min. at 300° F. with 1.5 parts BLE.

1a, 2a, 3a, 4a.

1b, 2b, 3b, 4b.

1. Unmasticated polymer.
2. Masticated 30 min. at 370° F.
3. Masticated 30 min. at 370° F. with 5 parts oxidized EPC black.
4. Masticated 30 min. at 370° F. with 1.5 parts BLE.

1a, 2a, 3a, 4a.

1b, 2b, 3b, 4b.

Fig. 8.

a large effect on these properties when mastication is carried out at 370° F. The effect of carbon black in the latter case is apparently due to its action in inhibiting gel formation.

OIL-EXTENDED POLYMER

A mastication time of 30 minutes at 300° and 370° F was used, as in the study with cold rubber, but the results were considerably different. The results obtained with GR-S-1710 (37.5 parts of oil per 100 parts of rubber) after 300° F mastication are shown in Figure 7. The drop in Mooney viscosity was much more marked with oil-extended polymer (OEP) than with LTP, and this drop was essentially unaffected by the presence of carbon black or BLE. Modulus and tensile strength were also lowered by the mastication, and again the additives produced little effect. The results with GR-S-1703 (25 parts of oil) were similar.

Only GR-S-1710 was tested at 370° F, and the results were in striking contrast to those obtained with cold rubber. The typical results (Figure 8) show mastication of oil-extended polymer for 30 minutes at 370° F to produce 18 per cent polymer gel, compared to about 40 per cent gel with cold rubber. The presence of carbon black and BLE, however, approximately doubled gel content in the oil-extended polymer, whereas in cold rubber gel formation was completely suppressed. This contrasting behavior extends to the physical properties of the vulcanizates as well. Whereas the presence of carbon black during the mastication of oil-extended polymer resulted in higher modulus and unchanged tensile strength, in cold rubber under similar mastication conditions modulus decreased and tensile strength increased.

It is possible that the very high molecular weight of oil-extended polymer is responsible for this reversal in effect. It is speculated that the mechanism involves the development of insoluble micro-carbon gel units produced by the adsorption of high molecular weight fragments.

BUTYL RUBBER

This polymer exerted its well-known resistance to oxidation under all the various types of mixing conditions employed. This finding is shown in Figure 9, which presents the results of mastication for 45 minutes at 225° F. Mooney viscosity was practically unaffected. The increase resulting from the addition of carbon black was about that expected from its direct effect on viscosity. Correspondingly, carbon gel and compounded physical properties were relatively unchanged with the exception that the presence of BLE tended to lower the properties of Butyl rubber.

The test results on stocks prepared from polymer masticated at 370° F are shown in Figure 10. The results are substantially similar to those obtained at the lower temperature. Mooney viscosity and carbon gel were again substantially unchanged, as were the physical properties of the vulcanizates. BLE, however, exhibited a more pronounced tendency to degrade the polymer than the cold mastication. Phenyl-2-naphthylamine also exhibited this behavior.

DISCUSSION

The action of carbon black in behaving as an antioxidant during Banbury mastication strongly suggests that a chemical reaction is taking place between the carbon and the polymer chains. As has been suggested previously⁶ this

Carbon black as an antioxidant in Butyl

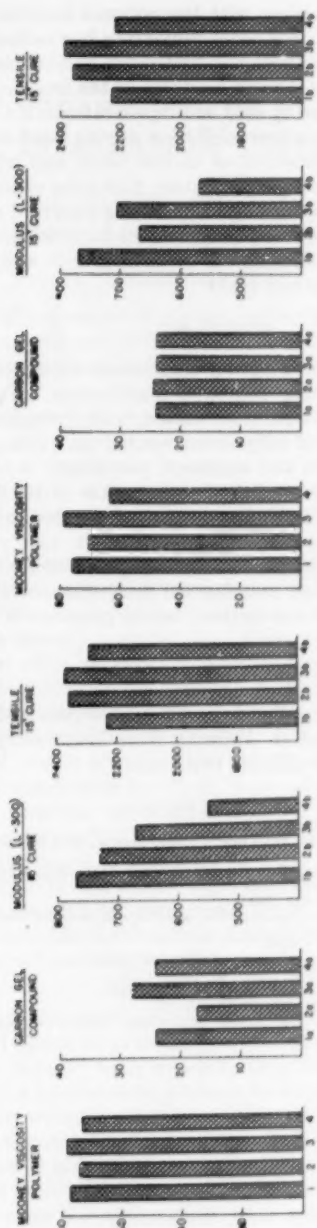


FIG. 9.

1. Unmasticated polymer.
2. Masticated 45 min. at 225° F.
3. Masticated 45 min. at 225° F. with 5 parts oxidized EPC black.
4. Masticated 45 min. at 225° F. with 1.5 parts BLE.

1. Unmasticated polymer.
2. Masticated 30 min. at 370° F.
3. Masticated 30 min. at 370° F. with 5 parts oxidized EPC black.
4. Masticated 30 min. at 370° F. with 1.5 parts BLE.

- 1a. 2a. 3a. 4a. Compounded stocks from 1, 2, 3, 4.
- 1b. 2b. 3b. 4b. Compounded vulcanizates from 1a, 2a, 3a, 4a.

FIG. 10.

reaction most probably takes place with the polymer free radicals produced by the initial attack of oxygen. Evidence indicating free radical interaction with carbon black has recently been presented by Garten and Sutherland². Watson¹⁰ has reported carbon black to act as an acceptor of the free radicals produced by the shear forces developed during cold mill mastication.

Although the effects of oxidation inhibition during Banbury mastication are measurable only with small amounts of carbon black and when mastication is carried out for relatively long periods of time, this type of oxidation inhibition by carbon black is undoubtedly taking place during standard mixing operations. The attachment of free radicals to the carbon surface, which most probably is responsible for the observed inhibition of oxidation, may well be a major factor in the reinforcing action of carbon black.

SUMMARY

Indirect measurements have shown that small amounts of carbon black inhibit rubber oxidation during Banbury mastication. To provide a more comprehensive picture of this inhibitory action, a study was made of its effects on some physical properties of fully compounded and vulcanized stocks prepared from masticated natural and synthetic polymers.

The action of carbon black, with the exception of its behavior in Butyl rubber, was found to be broadly similar to that of standard antioxidants. The largest change in vulcanizate properties occurred in cold rubber after high-temperature mastication. The usual shortening and stiffening resulting from gelation of the polymer at high mastication temperatures was completely inhibited when the mastication was carried out in presence of small loadings of carbon black.

ACKNOWLEDGMENT

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CONSTANT POWER PRINCIPLE IN ABRASION TESTING *

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INTRODUCTION

The assessment of resistance of rubber compounds to abrasion by laboratory methods is such a complex and difficult procedure that it is not surprising that a large variety of different methods has been developed and recommended in various laboratories.

Two aspects of the test have received attention.

Reproducibility, which involves accurate control over the dominant factors governing wear so that results can be satisfactorily duplicated on any rubber.

Validity, or the choice of such test conditions that the laboratory order of merit of a series of rubbers is not in conflict with their behavior under service conditions.

Various degrees of emphasis are placed on the necessity of the second of these requirements; the authors' views are that validity is a primary and indispensable factor by which a laboratory abrasion test should be judged.

It is becoming generally accepted that different service conditions are productive of different relative performances between rubbers, and Buist¹ and others have drawn attention to the need of a range of test conditions to cater for products such as tires, flooring, footwear, or clothing.

The most important application of rubber in industry still remains in treads of tires, in spite of the increasing diversity of other applications of rubber. Tire manufacture still accounts for about 70 per cent of the world's consumption of rubber, and since normal useful life of a tire is governed by wearing out or abrasion, the laboratory testing of resistance to abrasion might be regarded as the most important criterion of fitness for service. It is unfortunate, therefore, that the test proves to be one of the most difficult to carry out in such a way that the results can be used for prediction.

This paper concerns the development of a laboratory test intended primarily for assessment of tire-tread compounds.

HISTORY

Many empirical forms of laboratory abrasion-testing machines have been devised in the past, usually each concentrating on operation at fixed contact pressures and rubbing speeds as an attempt to simulate idealized service conditions. For example, we have the Akron angle-slip machine, Graselli Du Pont machine, Lambourn constant-slip machine, B.S.A.T.R.A. machine² as those which have been most widely used. A fuller list is given by Buist in his paper¹.

These machines were able to cope, to some extent, with the problem of assessing rubbers when the compounds were relatively few in number and

* Reprinted from the *Rubber World*, Vol. 132, No. 2, pages 201-210, May 1955. This paper was presented at the Third Rubber Technology Conference, London, June 1954.

widely different in properties. As compounding techniques progressed, it became increasingly important to differentiate between finer differences of abrasion resistance for the economics of production and service. The need of improving abrasion-testing methods became pressing.

Until 1932, Dunlop was using the Lambourn constant-slip machine³ as the best method for abrasion testing of tire-tread compounds. By this date, however, the differences between compounds of importance to the company had reduced to well within the test's discriminating power; yet there was service evidence to indicate the existence of real differences in some cases. In this period we frequently obtained inexplicable reversals of evidence in simple repetitions of straight compounding comparisons.

In a private communication⁴, Bruhat pointed out the suggestion arising from some results that constant slip alone was an insufficient control criterion for abrasion testing. When considering the lack of agreement between laboratory and road testing of abrasion loss vs. state of cure, he thought that the power passed through the rubber during abrading must be varying between successive tests.

In the Lambourn machine, adjustments to hold constant slip against any variations during a test were made by adjusting the power absorption in the brake³. In other words, transmitted power was deliberately altered, but not measured. Bruhat pointed out that where tests had been possible with constant brake current throughout the test series on a Lambourn machine, the repetition was very good.

This fact laid the foundation for considering abrading under some form of power control.

NEED OF POWER CONTROL IN A LABORATORY TEST

Extending the general view of a laboratory test outlined in the introduction, the same considerations must govern the principles of test design as are applied to the service information from the road. For example, results from differing service conditions are weighted to standard conditions to eliminate road, vehicle, weather, or driving variables. This is equivalent to controlling test-car schedules at specific rates of energy dissipation or power levels.

Controls on the laboratory machines must take care of these factors; yet the test must be short. All abrading actions are complex, but the fierceness of the action can be assessed by considering the energy dissipated at the rubbing faces, whatever the nature of the mechanism of surface removal.

Hence, after the nature of the surfaces to be rubbed together at a selected relative speed has been decided upon, the remaining complex abrasion factors can be standardized by controlling the power transfer of the system.

In other words, abrasion machines should operate under constant power conditions.

The work of the authors on machines designed to operate on this principle has led them to support the view that any existing design of machine is certain to be improved in test performance by introducing energy control or correction. Williams⁵ also took a similar view in his original paper on the du Pont abrader.

DISTRIBUTION OF POWER IN ABRASION MACHINES

In order to cause one surface to abrade another, an input power P_1 is necessary immediately next to the input side of the abrading interfaces. The power is distributed throughout the abrasive/test-piece system thus:

4.1 Both surfaces moving, but having a relative slip velocity:

$$P_1 = P_R + P_T \quad (1)$$

4.2 Output surface at rest, slip velocity arising only from the movement of one surface:

$$P_1 = P_R \text{ (and } P_T = 0 \text{)} \quad (2)$$

Where P_R = power absorbed into the surface materials as abrasion power and heat loss.

P_T = power transmitted through the interface to appear as work against a load driven by the mechanism.

The Lambourn and Akron angle machines⁶ operate as type 4.1; while the du Pont and U. S. Bureau of Standards machines operate as type 4.2.

Also in type 4.1, if F = force acting, and V = velocity of output surface, then:

$$F = P_T/V \quad (3)$$

Let v = relative rubbing or slip velocity between the surfaces; then:

$$P_R = P_1 - P_T = F[(V + v) - V] = Fv \quad (4)$$

From (3) and (4) $P_R = P_T v/V = (\% \text{ slip}/100)P_T$ in Lambourn slip notation. (In practice, measurement of power differences include rubber losses and some bearing losses, as well as P_R .)

Therefore tests at constant transmitted power through a constant slip drive give fairly complete control of all the energy factors of the system.

CONSTANT ENERGY METHODS

The rate of energy dissipation in the test-piece can be controlled by alteration of either force or slip at the rubbing surfaces. In most machines the slip is maintained constant, giving a constant speed for the power control device.

Typical methods for five types of machine are now discussed.

(1) ROTATING TEST-PIECE DRIVING A ROTATING ABRASIVE WHEEL (E.G., LAMBOURN MACHINE)

It is necessary to fix the speed of the output shaft; then apply a constant brake-torque on this shaft to obtain constant transmitted power. Windage and friction losses are constant by virtue of the constant speed.

(2) FIXED TEST-PIECE PRESSED AGAINST CONSTANT-SPEED ROTATING ABRASIVE WHEEL (E.G., DU PONT AND NATIONAL BUREAU OF STANDARDS MACHINES)

Here all that is needed is a control for constant tangential force on the test-piece carriers.

(3) TEST-PIECE MOVING IN CONTACT WITH A FIXED ABRASIVE SURFACE (E.G., B.S.A.T.R.A. MACHINE)

In this type, the test-piece can be made to move at constant surface-speed, and the forces on the abrasive surface member measured and kept constant.

In each of these cases the most convenient method of control to hold both power and slip constant is by relatively very small adjustments of test-piece

know the exact power transfer picture. It would be necessary to measure torques or tangential forces on each of the drives to the two surfaces. The two surface velocities would need to be controlled to be constant.

DUNLOP CONSTANT-POWER LAMBOURN MACHINE

A description follows of one interpretation of the constant-power principle applied to a Lambourn-type machine.

Figure 1 is a schematic block diagram, and Figures 2 to 5 show general views of two forms of this type of instrument.

Mechanically, the machine retains the principle of a rolling test-piece driving a braked abrasive wheel, except that the test-piece runs on the edge of the wheel, not the face⁷, a feature adopted in the later forms of Lambourn constant-slip machines. Provision is made for mechanical measurements of input power for calibration of the brake.

Also provision is added for adjusting and steadying the test-piece pressure on the abrasive. Slip level is adjusted by this method throughout the test.

Electrical features are:

(1) Very accurate speed control of the abrasive shaft by phase control derived from 50 cycles a.c. mains fed to a second eddy current brake fitted to the motor spindle. The circuit is based on a design by Bulgin⁸. A series motor is essential for this type of control. Variations of speed are no greater than those of the a.c. mains frequency.

(2) Stabilized current supply to the abrasive shaft brake to govern transmitted torque.

(3) Continuous display of slip ratio by a stroboscopic system, operated from a light idler pulley running on the test-piece surface.

(4) Automatic cycle controlling and timing to simplify routine operation.

Trouble has been experienced in abrasion testing of some rubbers with stickiness on the test-piece surface. This gives fictitiously low loss figures by causing particles to remain on the test-piece, in extreme cases appearing as rolls on the surface and clogging the abrasive surface. The effect is considerably reduced by controlled carborundum grit feed to the rubber-abrasive nip. Because of this, the later designs of machine (Figures 3 and 4) are arranged with the nip vertical. Special tests on other feed materials and devices are in Appendix A.

The abrasive is provided by "36-grit" carborundum wheels, with fresh-fired surface (not redressed or trued after firing). These give a useful life of up to six months by using half of the full edge width to give two tracks by wheel reversal.

The main dimensions of the test-piece and the abrasive wheel are the same as in the original Lambourn machine: test-piece: $1\frac{1}{2}$ -inch diameter by one centimeter wide, with a splined steel center; abrasive wheel: seven-inch diameter by one inch wide by $\frac{1}{4}$ -inch hole.

TEST METHODS

Each test-piece is given a rough grinding on a separate device to assure concentricity, followed by a period of running on the abrasion machine itself to align the test-piece surface truly with that of the abrasive wheel.

A complete comparison of compounds involves four runs of five minutes for each test-piece, arranged on a randomized statistical plan for the testing to minimize the effect of abrasive and rubber variations.

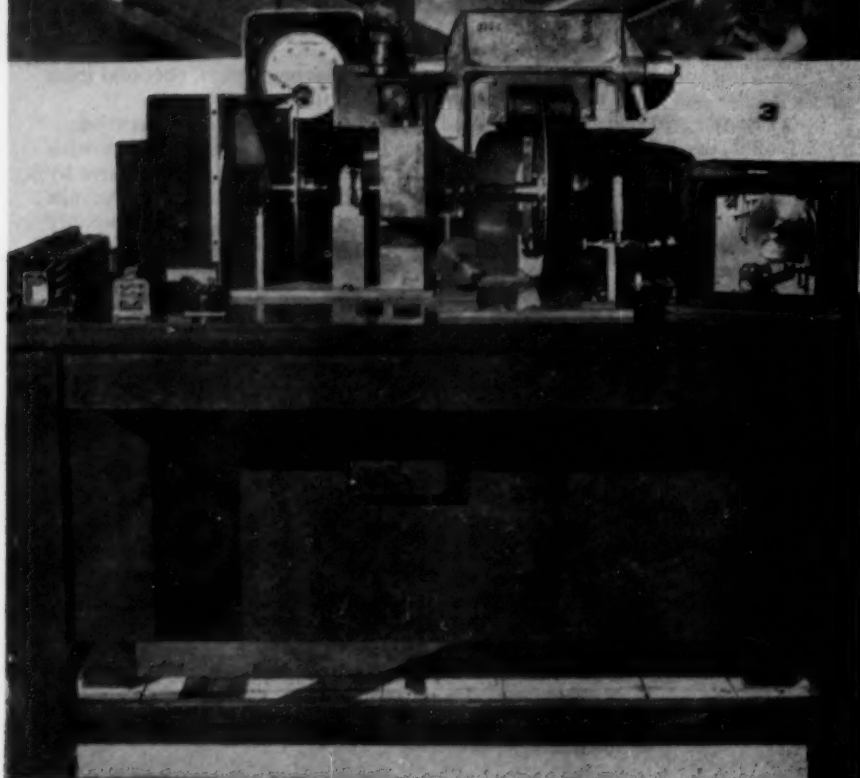
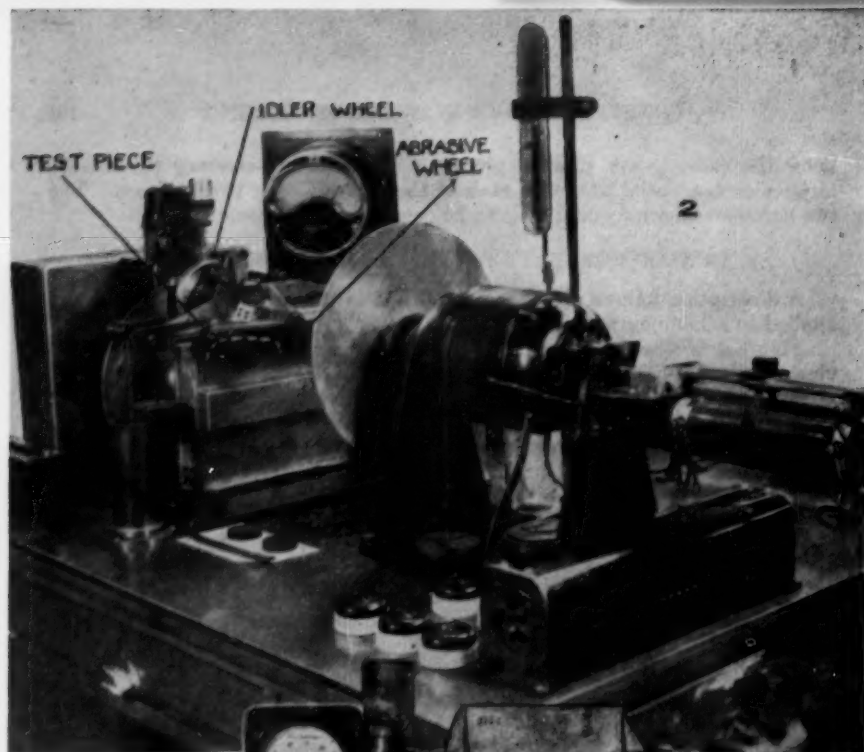


FIG. 2.—Original horizontal beam machine. Test-piece and abrasive wheel are behind housing in locations indicated by dotted lines.

FIG. 3.—General view of vertical nip machine.

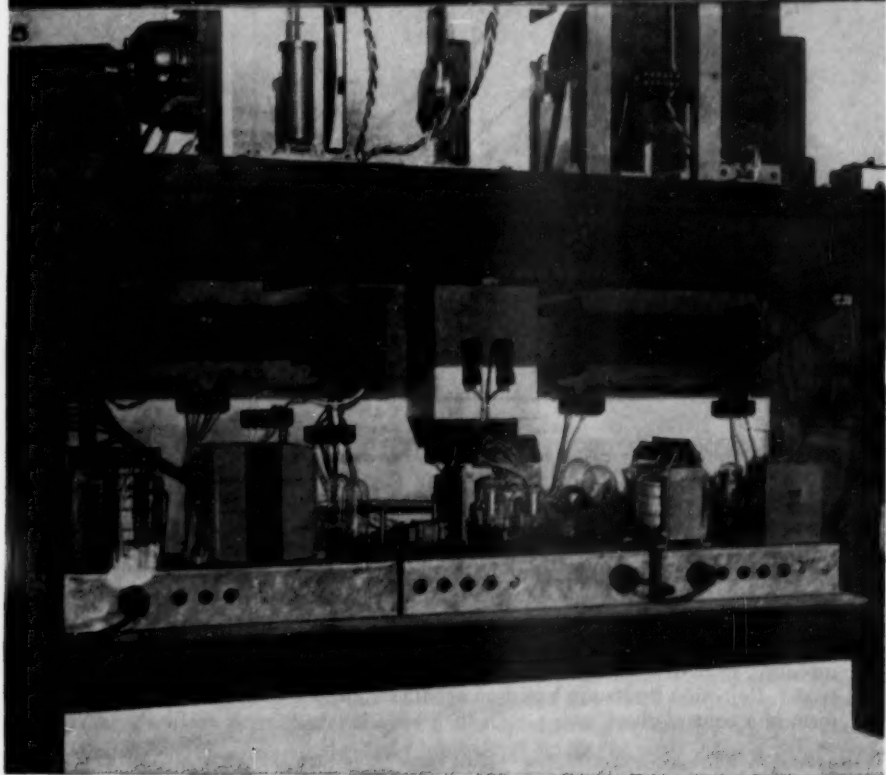
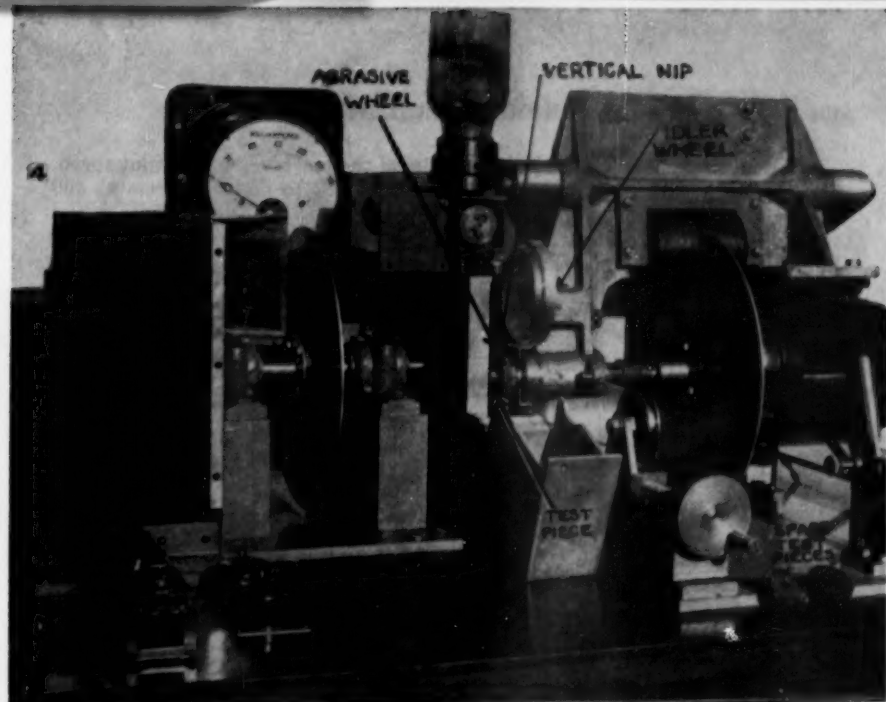


FIG. 4.—Vertical nip machine, showing test-piece and idler pulley.
FIG. 5.—Control cabinet at rear of machine.

The mechanical and electrical constants of the machine, e.g., output speed, brake current, slip ratio, are set at levels designed to make all tests at 400 kgm.-cm./sec. transmitted power, with a slip ratio of 16 per cent. These values were chosen so that the machine will run in a stable manner with some reserve for control and still place the greatest number of compounds in the order of merit found to exist in service. The test conditions can be varied, however, over a wide range whenever such variation is desired.

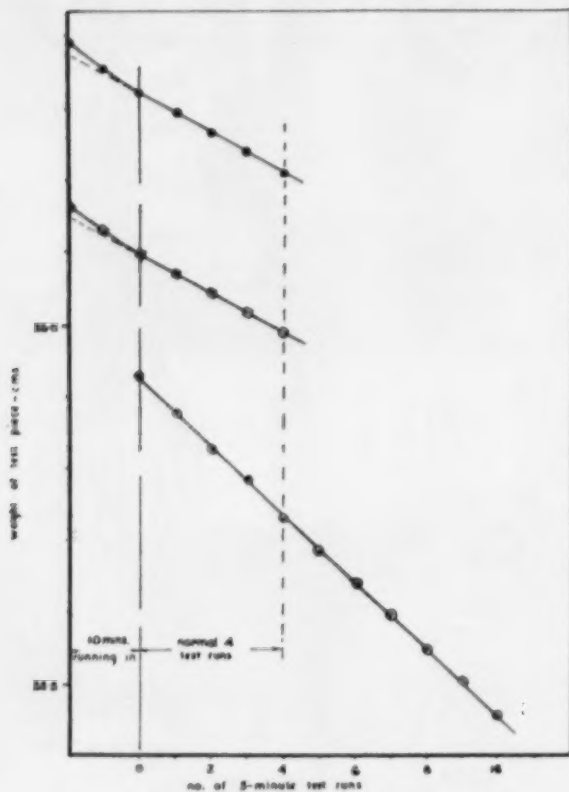


FIG. 6.—Typical test-piece weight losses during successive runs.

REFERENCE COMPOUND

Every comparison group is arranged to include a test-piece from a batch of a standard reference compound, and all volume losses are referred as resistances to wear relative to the reference compound test-piece on a percentage basis. A fairly large batch of the reference compound is mixed at a time, and the test-pieces are cured in groups of 12 to 24 from this batch. Before being put into use, each fresh batch of reference test-pieces must pass an acceptance trial. Rejection limits are based on accumulated evidence of test error, in the form of a control chart.

SPECIAL TESTS

In order to assess possible effects of other variables, a number of special investigations were made. These are outlined in Appendix B.

GENERAL PERFORMANCE OF THE MACHINE

A number of these machines have been built in different Dunlop laboratories; the first two still are in use after 20 and 16 years, respectively. Five

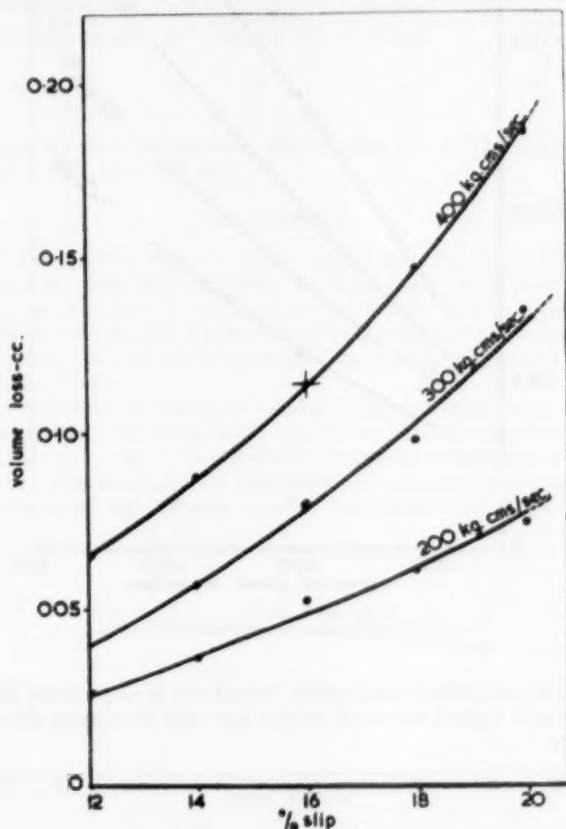


Fig. 7.—Typical volume loss vs. percentage slip.

more of the No. 2 type—with the abrading nip arranged vertically—have been brought into use during the last 8 to 10 years. The last two are somewhat improved in details, particularly the electrical and electronic controls, but are still based on constant transmitted power at constant-slip ratio.

The rate of wear of a test-piece with time during a test run, under the standardized conditions, is linear except for the running-in period. The preliminary running-in insures that the true test run does not commence until the linear condition is reached. Figure 6 illustrates this graphically.

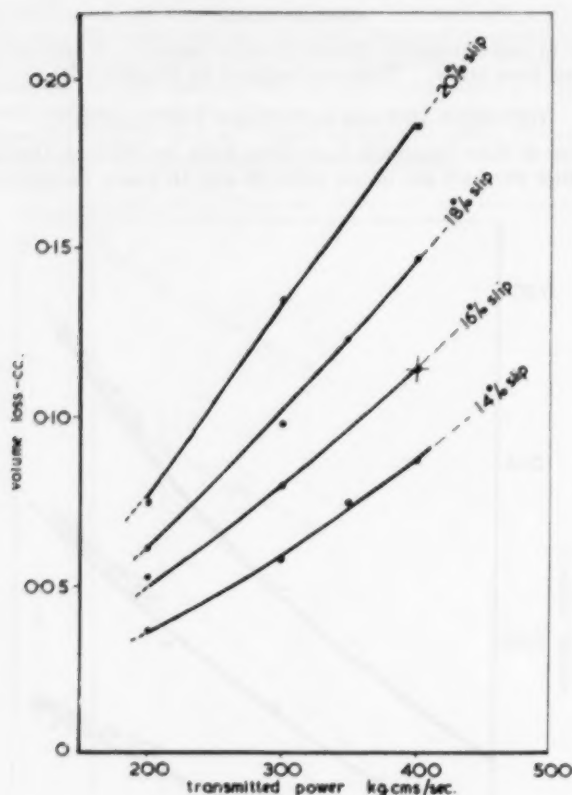


Fig. 8.—Typical volume loss vs. transmitted power.

The need of controlled standardized conditions is emphasized in Figures 7 and 8, which give typical curves of volume loss with percentage slip and transmitted power.

WHEEL LIFE

During a series of tests, the sharpness or effective abrading power of an abrasive wheel falls away gradually. This point is shown in the typical life curve of one compound on two abrasive wheels given in Figure 9. The testing technique already described is designed to minimize this effect. As shown by the broken line curve of Figure 9, redressed wheels have an impracticably short useful life. By arrangement with the manufacturers, specially true-running fresh-fired wheels are used. The wheels are rejected after becoming blunt. They are not redressed and used again. When new wheels are brought into service, it is advisable to check their performance by first testing three or four different compounds of known abrasion indexes.

REPRODUCIBILITY

Error variability is continually examined by control chart methods. It varies with weight loss and abrasion index, as shown in the representative table below.

LEAST DIFFERENCE REQUIRED FOR SIGNIFICANCE BETWEEN TWO COMPOUNDS AT A PROBABILITY LEVEL OF ONE IN 20

Abrasion resistance of highest of pair of results Ref. compound = 100	Mean weight loss of reference compound		
	100 mg.	80 mg.	60 mg.
80	5	6	8
100	8	9	12
120	11	13	17

It is customary to reject abrasive wheels when the weight loss of the reference compound falls below 50 mg.

CORRELATION

It is a long and difficult task to obtain enough data for an adequate correlation between road wear and laboratory abrasion loss. It is very rarely that enough vehicles and tires can be used exclusively for this purpose. Results often have to be collected from many small independent experiments and dealt with as statistically as possible to determine the most probable road correlation for the laboratory test.

Figure 10 shows the correlation obtained from one fairly large experiment run under controlled conditions, using test-pieces from the actual treads which were run on the road. It will be noted that there is substantially a 1:1 relation. It is found that differences usually exist between laboratory mixed and production mixed rubbers, and between molded test-pieces and strips from tires.

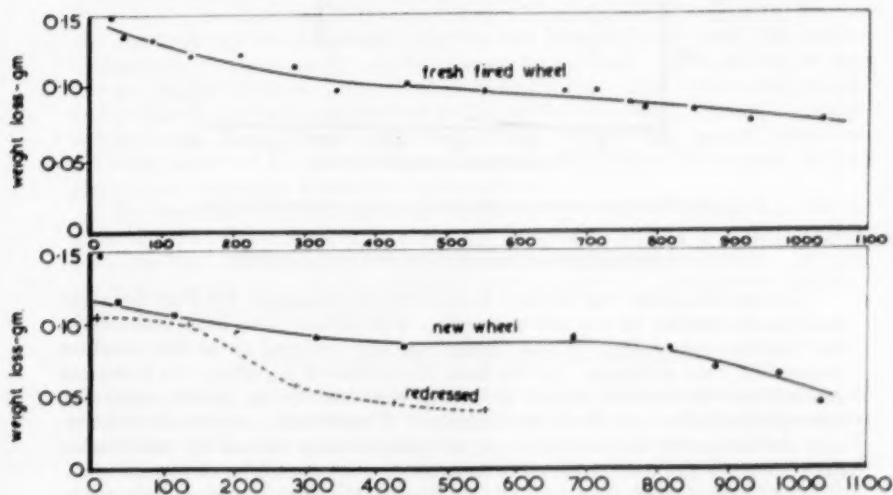


Fig. 9.—Typical weight loss—number of runs during life of abrasive wheels.

Allowances for these have to be made when predicting road performance from laboratory mixed and cured test-pieces. The general effect is to increase the slope of the equivalent line of Figure 10 in the direction of greater sensitivity for laboratory molded test-pieces.

APPLICATION OF CONSTANT POWER TO OTHER MACHINES

It has already been pointed out that any abrasion machine can be improved by adding power controls, and some tentative methods are given. Following this idea, two other machines have been converted to operate on these principles in the authors' company.

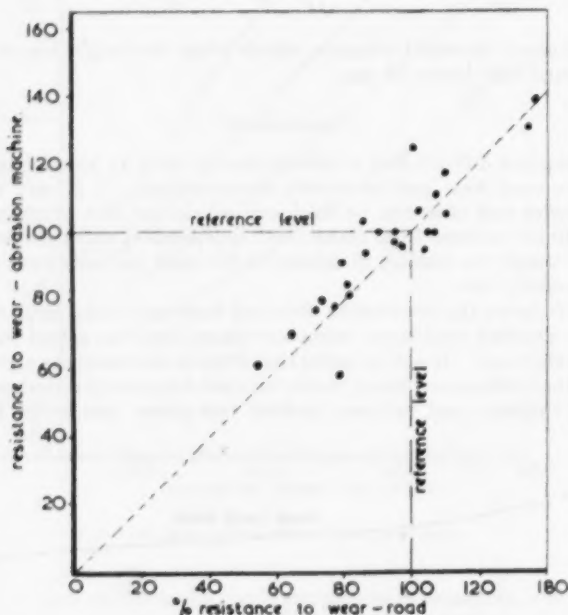


Fig. 10.—Road correlation strip test-pieces from road-test tire covers.

CONSTANT-POWER DU PONT-TYPE MACHINE

This modification⁹ was devised to convert any standard Du Pont abrasion machine to operate on the new principle. Full details have been disclosed at the Conferences of ISO/TC/45 Committee and referred to as the constant torque Du Pont machine. In the main it consists of adjusting the test-piece pressure on the abrasive wheel by a pull wire and spring system extending through the hollow spindle of the machine. The adjustment is made to maintain the torque on the test-piece carrier arm constant judged by free floating between stops against the reaction weights on the extremities of the arm.

The improvement in results on the Dunlop-Du Pont machine is shown in the following table.

Compound	Constant torque	Constant load	Load
A	100	100	100
B	92	145	92
C	85	159	80
D	73	100	75
E	63	54	75
F	38	50	59

CONSTANT-POWER U. S. BUREAU OF STANDARDS-TYPE MACHINE

This machine is not yet completely evaluated. It consists of five test-piece carriers, each on arms arranged to act as bending cantilevers against the torque action of the rubber held against the moving abrasive wheel surface. The forces on the cantilevers are measured electrically.

The machine is very simple to operate, capable of testing very small rubber test-pieces, but its performance and best applications remain to be assessed.

THE MECHANISM OF ABRASION DAMAGE TO RUBBER

In seeking ways to improve abrasion resistance by compound or choice of polymer, it would be of great value to understand more fully the exact mechanism of surface removal and what forces and energies are involved. Buist and Davis¹⁰ have attempted to establish correlation between other physical properties, more readily measurable, which has, however, limited validity. A more fundamental approach has been reported by Schallamach¹¹.

It is interesting to examine work published on metal grinding, where a study was made of energy dissipation and temperature effects. A summary of this work relevant to the rubber abrasion problem follows.

THE GRINDING OF METALS

Work published by Shaw and others¹² has established the general rule that the energy required to remove unit volume of a crystalline material like a metal by grinding or abrasion (defined as the specific energy) increases as the size of the removed particle decreases. As the size becomes very small (20 micro-inches), the specific energy approaches an upper limit corresponding to the energy required to shear lines of atoms in the metal. This critical size proves to be that of the local irregularities in the crystal structure. Extending these principles to more general abrasive systems, the specific energy would be expected never to be greater than a value corresponding to rupture of the atomic and molecular structure of the material.

The importance of this approach in laboratory abrasion testing of rubber is in connection with attempts to speed up the rate of testing by using coarser abrasives and higher input power than the product meets in service. Larger particles are torn out, and the specific energy per unit volume removed is likely to be much lower than in service.

DISRUPTION ENERGY OF A RUBBER STRUCTURE

It is difficult to calculate the maximum value of the specific energy of a rubber structure. The ultimate theoretical mode of failure might be taken as disruption of all bonds and reduction to isoprene monomer, in the case of natural rubber and to free particles of filler. This then involves an energy consumption equal to one C—C bond per isoprene unit, plus the heat of wetting of all compounding ingredients used. Further energy would have to be allowed

for secondary bonds or van der Waals type forces between chains. This can be estimated from activation energy of plastic flow, or from the free surface energy of unsaturated hydrocarbons.

Some calculations on these lines are given in Appendix C, and the conclusion drawn is that the maximum energy needed to create new surface by abrading rubber is theoretically of the order of 2000 ergs/sq. cm.

Using experimental figures for the size of the particles from two typical laboratory machines, an estimate is made in Appendix D of the theoretical maximum energy required to tear out particles from the rubber.

The figure thus derived is about

$$2.1 \times 10^6 \text{ ergs/cc. volume loss}$$

or

$$0.5 \times 10^{-4} \text{ kgm.-cal./cc. volume loss.}$$

Comparable experimental energies required in various abrasion systems are given below.

Type of abrasion	Typical energy dissipated per unit volume loss (kgm.-cal./cc.)
Constant energy Du Pont machine	5.4
Lambourn machine	4.1
B.S.A.T.R.A. machine ¹²	0.25
Rubber brake blocks on smooth cycle rims	1000
Rusty cycle rims	100
Automobile brake shoes on smooth drums ¹⁴	850
Cornering of tires on cars	1 to 25

CONCLUSIONS FROM ENERGY CALCULATIONS

The most striking conclusion from these figures is the completely insignificant part which the structure bond energy plays in the practical energy levels required for abrading rubber. Even the most vigorous abrasion machine (B.S.A.T.R.A.) gives a figure of 5000 times the bond energy.

By comparison, the behavior of a crystalline metal shows a much closer correspondence with the theoretical energy under fine grinding conditions. The general effect of a large rise of specific energy of abrasion with increasing smoothness of rubbing agent is found in both cases.

In frictional rubbing, therefore, it seems that the great bulk of the work done is by repeated deformation of thin surface layers and consequent energy conversion by the asperities of the rubbing agent, without breakage of the structure. Only in extreme cases of interference of the surfaces are particles broken off and removed from the scene of action. Expressed briefly, it is therefore possible to visualize friction without wear, particularly on very smooth surfaces.

A further practical conclusion is that the ability of a rubber to deform and absorb large quantities of work at high temperature without fracture is the property which governs abrasion resistance. This suggests that possibly tensile product (breaking load \times breaking elongation) measured at 150° C or higher, combined with fatigue resistance to rapid stressing, might be found to correlate with wear resistance.

OXIDATION EFFECTS AT HIGH TEMPERATURE

The temperature and oxidation phenomena in metal grinding are very important in the energy exchange.

Local temperatures were shown¹² to be in the region of the melting point of steel, though difficult to measure. The glowing sparks from some metals were shown to be due to oxidation heating after leaving the nip.

Experiments on grinding steel in inert gas showed greatly increased forces and a large rise of specific energy, due to rewelding of chips to the parent metal and the necessity of repeated cutting of the same piece of metal.

In the case of rubber, although the disruption energies involved are lower than those of metals, it is very probable that the abrasive action involves temperatures at which physical properties are very much degraded, compared with their normal values. Furthermore, oxidation at these temperatures would lead to a sticky product, and the "chips" or ground powder would be more likely to adhere to the parent sample and cause a reduction of abrasion loss.

We have, therefore, almost the opposite case from that of metals, and it might be thought that a laboratory test in a nitrogen atmosphere would offset the stickiness problem due to excessive temperature and make the abrasion mechanism a closer approach to service conditions.

Experiments on these lines are reported in Appendix A. The use of nitrogen failed to eliminate stickiness, but this condition may be due to the great difficulty of removing the last traces of oxygen. The important suggestion remains that the chemical nature of the rubber in relation to oxygen is a vital factor in the mechanism of abrasion.

Possibly experiments in oxygen-enriched atmospheres may yield valuable information on polymers which are less readily oxidized than natural rubber.

SUMMARY AND CONCLUSIONS

This paper has been mainly concerned with presenting the case for power control in abrasion testing, and the implications of the better understanding of the mechanism of abrading. It is not claimed that the test machines described are perfect in their ability to assess resistance to wear action. There is still much to be done to remove anomalies that can still occur in results.

One underlying principle, that of constant rate of energy dissipation at the abrading surface, is proposed as a criterion for comparison of the validity of test design for the many different types of laboratory test in regular use for assessment of wear resistance.

Modification of the Lambourn constant-slip machine to make it conform with the constant-power principle is described, and the degree of correlation with service data on tires given.

The effects of several major variables on the abrasion loss of rubber tread compounds, when tested with the modified Lambourn machine, are reported, including work on combating stickiness.

Experiments with the Du Pont and U. S. Bureau of Standards abraders, modified to conform to constant-power principles, are also reported in this paper.

The relations between work done in mechanically grinding rubber and the energy associated with the bonds ruptured in the grinding action are considered. It is suggested that a correlation may exist between abrasion and high-temperature flexibility properties of rubber.

ACKNOWLEDGMENTS

The work reported in this paper has been active over a long period, and embodies results provided by many of the authors' colleagues. In addition to

those referred to in the paper, we must acknowledge special gratitude to D. Parkinson for his continued support and interest, to B. J. A. Martin, C. H. Leigh-Digmore, and B. Pickup for more recent data and valuable criticism, and to C. E. Kendall for advice on more fundamental chemical matters.

Thanks are also due to the technical director of Dunlop Rubber Co., for permission to publish the work.

APPENDIX A

COMBATING TEST-PIECE STICKINESS

Stickiness has been experienced by all workers on abrasion. While, in the early days, only a few compounds seemed to exhibit this effect, most modern compounds are affected to some degree. When stickiness exists, abraded particles do not leave the test-piece, but remain adhering to the sticky surface to be rolled repeatedly under the abrading contact. The final measured weight losses are then fictitiously low for the purpose of abrasion assessment.

Many devices were explored to combat this phenomenon; none was completely successful for all compounds. These are listed below:

- | | |
|---|---|
| 1. Water spray into the nip. | Weight losses extremely low, 2-3 mg. in one hour. |
| 2. French chalk into the nip. | Weight losses extremely low, 1-2 mg. in two hours. |
| 3. Scrapers on the test-piece. | Aggravated the stickiness. Rolls not removed. |
| 4. Fixed wire brushes on the test-piece. | Tended to increase stickiness without removing rolls. |
| 5. Fixed bristle brushes on the test-piece. | |
| 6. Rotating bristle brushes on test-piece. | Removes drier detached particles—no effect on rolls or stickiness. Adopted as on original machine. |
| 7. Finer grit abrasion wheel. | Aggravated the stickiness. |
| 8. Emery flour into the nip. | Weight losses extremely low. |
| 9. Emery grits into the nip. 36, 60, 120 mesh (and mixtures). | Weight losses rather variable. |
| 10. Enclosing test apparatus in an inert atmosphere—nitrogen. | Even after careful flushing out remaining air, after evacuating many times, with N_2 , and similar treatment of the rubber test-pieces, stickiness still occurred to the same degree as normal testing. (Possibly traces of air still present in spite of treatment.) |
| 11. Carborundum grits into the nip. | Grit size too large for easy governing constant flow. |
| 12. 36-grit carborundum. | |
| 13. 120-grit carborundum.
120-grit Crystolon. | Weight losses uniform. Flow controllable constant. Satisfactorily removed stickiness for many compounds. |
| 14. 80% 120-grit Crystolon ¹³ and 20% emery flour. | Weight losses still uniform. Removed stickiness to a greater degree and handled more compounds than 13. |

Method 14 was adopted, but there are still some rubbers which are too sticky for reliable abrasion results. The practical answer is that any grit which can be guaranteed for size and hardness of this order of mesh should be satisfactory if fed at constant rate close into the nip.

Attempts to correlate compound constituents with stickiness have not proved very convincing.

APPENDIX B

SPECIAL TESTS

Ambient temperature and abrasion.—Using the same enclosure system devised for the nitrogen tests (Appendix A), tests were made under ambient temperature conditions over the range 20° to 100° C.

The weight loss on the natural-rubber tread compound tested increased linearly with temperature. This is shown in Figure 11, together with the reciprocal curve of resistance to wear vs. temperature.

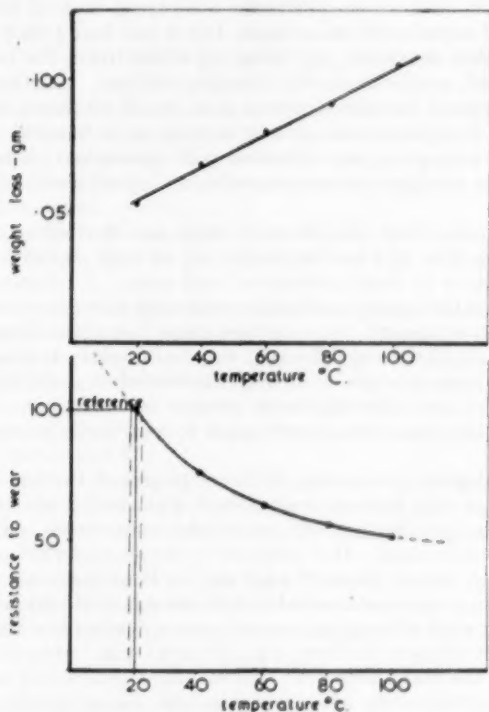


FIG. 11.—Effect of ambient temperature on abrasion of natural rubber tread.

On this evidence, since the main testing laboratories change temperature over a wide range during a few months, it was decided that the abrasion machine should be operated in the special controlled temperature laboratories ($20 \pm 2^\circ$ C).

Half and half centers.—A half lap split steel center was devised to enable half test-pieces to be built from two rubbers of a comparison. This was thought to be a possible equivalent of the road test and half treads which are frequently used in investigations as a method to reduce some road test variables.

This design of test-piece was not successful, the slip ratio for a given beam load setting being different for each half wheel. The slip stroboscope image

remained steady due to the rotary inertia of the test-piece drive, and the test run was made at a mean slip of 16 per cent. The energies and slip on each half, however, are not equal; hence, the two halves are not tested at strictly standard conditions. The practical effect was to reduce the differences between compounds to an unacceptable level.

Half-and-half test covers may suffer from a similar interaction, rendering road evidence from these tests less valid than is usually assumed.

Pneumatic test-piece.—Following a suggestion that a more flexible test-piece construction may make for less variability, a simple hollow inflatable rubber test-piece wheel was designed, small enough to fit the existing machine (i.e., 2½-inch diameter) with a one-centimeter wide tread molded integral with it.

A number of experiments were made, but it was found that variability increased rather than decreased, and crowning of the tread, due to the increased flexing under load, produced an ever-changing stiffness. Further, it is difficult to maintain constant inflation pressure in so small a volume, due to leakage difficulties, and this constitutes another control to be handled. Best results, and even these were poor, were obtained with atmospheric inflation pressure. Mechanically the machine ran very smoothly and silently with this type of test-piece.

It was concluded that the effects of test-piece flexibilities and stress encountered in this type of wheel are better left to tests on full-scale tires using larger apparatus, or to detail analysis of road tests. A laboratory test of the type dealt with in this paper is primarily concerned with determining the resistance to wear of a compound, not test-piece shape factor and design effects. To deal with these product design effects, it may be necessary to apply corrections, based on results from separate study of the factors when predicting performance of a compound in two different tire or product constructions. This does not affect the separate conception of resistance to wear index of the compounded rubber.

Abrasive materials.—Originally, abrasive papers of the water glue bonded type were tried in strip form on a seven-inch diameter by one inch wide drum. These were very variable ($\pm 10\%$ on weight loss), owing, no doubt, to the weakness of the glue bond. It is proposed to reopen this work using the newer Tri-M-ite (I.S.O. batch) papers¹⁶ used on Du Pont machines in due course. This may lead to a more economical system for standard abrasive surface.

Early in the work of applying constant energy principles, the possibility of more permanent abrasive surfaces, e.g., diamond grit, boron carbide grit, was discussed with the manufacturers. No standard production of suitable grit size wheels (approximately 36-grit) exists, and special production would be prohibitive in price. The price, however, could be secondary in importance if these types of wheel proved to be more permanent. Experiments with existing fine diamond dust wheels proved useless; these simply aggravated stickiness. Development of this approach was not carried further.

APPENDIX C

ENERGY REQUIREMENTS FOR BOND BREAKAGE

Considering the ultimate unit likely to be involved in the finest possible abrasion action as the isoprene unit in the rubber chain, the bonds holding these in place are regarded as consisting of one covalent C—C bond per isoprene unit, the associated secondary van der Waals type forces between adjacent side groupings, and an occasional vulcanization cross-link.

The orientation of the isoprene units with reference to any particular plane of possible rupture is random in unstressed rubber, but the act of stressing increases the degree of orientation normal to the plane of rupture.

Assuming first that all the bonds are fully orientated, the maximum number of covalent bonds will need to be broken, i.e., one per isoprene unit present at the new surface created.

Taking the C—C bond strength as 80 kcal./mole, and the size¹⁷ of the isoprene unit cell normal to the main chain as 27\AA^3 , we get:

$$\text{Energy per molecule} = \frac{80 \times 4.185 \times 10^{10}}{6 \times 10^{23}} = 5.6 \times 10^{-12} \text{ ergs.}$$

$$\text{and energy per sq. cm.} = \frac{5.6 \times 10^{-12}}{27 \times 10^{-16}} = \text{approx. 2000 ergs.}$$

Now, in the case where rupture occurs so that no covalent bonds are involved, but only the secondary bonds, the figure may be taken as approximately twice the free surface energy (i.e., twice the surface tension figure for simple unsaturated hydrocarbons). This gives about 60 ergs/sq. cm., a much lower figure than that above.

The stress at the region of rupture will increase the orientation in the direction of stress, so that a high proportion, say 50 per cent, of the strong bonds will be involved.

The effect of carbon black reinforcement is a further increase in the work to be done on bond breakage. Judged by increase in tensile strength, the increase is 1.5:1 for natural rubber, and as high as 4:1 for butadiene-styrene rubbers, compared with the gum stock. Judged by increase in resistance to wear, the effect of blacks is as much as 4 or 5:1 for a fully reinforcing black under some types of wear conditions¹⁸. For the purpose of this estimate, we will take the carbon black factor as 2.0.

The effect of the occasional cross-links between chains due to vulcanization can be ignored, because it is probable that the ultimate plane of failure will divert to follow the weaker portions of the molecular network which exists between cross-links.

We may speculate, therefore (and the simplified assumptions do not warrant any stronger word), that the maximum theoretical energy attributable to bond destruction in creating each sq. cm. of new surface is of the order of

$$2000 \times 0.5 \times 2.0 = 2000 \text{ ergs/sq. cm.}$$

for a carbon black reinforced rubber.

The use of plasticizers which may be regarded as increasing the lateral spacing of chain segments will have the effect of reducing this figure, as van der Waals forces will be reduced, and the number of strong bonds in the plane of rupture will be decreased.

APPENDIX D

INCREASE OF FREE SURFACE AREA INVOLVED IN ABRASION

In order to use the energy figure calculated in Appendix C, it is necessary to estimate the amount of new surface created in grinding off a unit volume of material, and this is obviously dependent on the particle size.

Consider the particle to be approximately cubical of side x . In its original position five of the square faces are bonded, and one free. These five faces

must be broken to free the first particle, but subsequent adjacent particles need only four faces to be broken. The total area increase for a large number of small particles is, therefore, only $4x^2$ to a close approximation.

In unit volume, number of particles $N = \frac{1}{x^3}$ and increase of free surface is $\frac{4}{x}$ sq. cm./cc.

Measurement of particle size distribution from laboratory abrasion machines gives the following data.

	Du Pont (constant energy)	Lambourn type (constant energy)
Mean particle size number ($m\mu$)	40	37
Range of size ($m\mu$)	10-250	5-300

(The harmonic or reciprocal mean was taken in order to use the figure in calculating the surface.)

Taking 38 $m\mu$ as an average for the two machines, the new surface for unit volume loss is:

$$\frac{4}{38 \times 10^{-4}} = 1050 \text{ sq. cm./cc.}$$

REFERENCES

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- ¹⁶ Manufactured by Minnesota, Mining & Mfg. Co., Birmingham, England.
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CUT GROWTH AND FLEX TESTING OF NATURAL RUBBERS AND SYNTHETIC ELASTOMERS *

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I. INTRODUCTION AND DISCUSSION OF PREVIOUS METHODS

In the last decades, numerous studies¹ have appeared concerning the behavior of tears in natural rubber and synthetic elastomers. In the United States² and England³ there are even standardized test methods. It can be seen from all the investigations and test instructions that the results are very poorly reproducible and only rarely agree with practical experience.

In investigations on the behavior of tears, the two stages—the beginning of the tear and the growth of the tear (tear propagation)—must be differentiated. The following factors must be given primary consideration in starting the tear: external damage, the action of ozone and oxygen, frequently changing tensile or compression stresses. Here oxygen plays a role similar to that in the corrosion of metals. Fatiguing mechanical stress undoubtedly leads to the appearance of tears. But it can be assumed that the beginning of a tear observed in the area of maximum stress takes place at a *preferred* point on the surface. Such preferred points are always present. As is well known, the surface of a material—even on a high polymer—must not be regarded as completely “smooth”. In place of this supposed smoothness, there appears under microscopic or electron-microscopic observation a kind of “mountain system”. Observed under sufficient magnification, the “valleys” or cuts in the mountains are comparable to tears. Under mechanical stress, such cuts will then continue to grow particularly rapidly (nick effect). Now it is largely dependent on the kind of observation and the observer as to whether a small irregularity in the surface is called a tear. The beginning of the tear cannot, therefore, be defined clearly. The case is quite different with tear growth. The initial conditions—the tear present at the beginning of measurement—are given and only the growth of the tear has to be followed by measurement. The growth of the tear therefore seems to us to be well suited for detailed investigation.

Almost all previously published papers concerning the tear behavior of elastomers refer to tests carried out with De Mattia, Du Pont, Scott, or Flipper testing machines⁴. These machines subject the test substance to a continuous mechanical stress (tension, compression). With some of these machines the *magnitude* of the stress in the test can hardly be determined. The test results with different machines can, therefore, be compared only with difficulty. Even with the internationally recommended De Mattia machine, there are considerable difficulties in specifying the magnitude of the tensions produced. The front of the test strip, which has a groove⁵ vulcanized into it, is extended on bending, as can be seen from Figure 1c. It is not possible to measure the ten-

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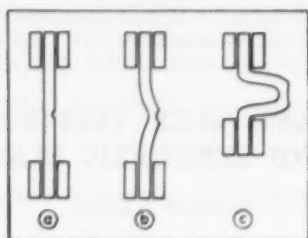


Fig. 1, a-c.—Most usual arrangement for the bending test of a tear. a and b—different lengths between clamps. c—test-piece stressed. Side view, schematic.

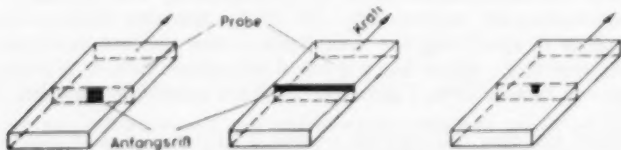
sion in the groove exactly⁶. Furthermore, the bending—and thus the tension—depend largely on whether the length of the test-piece corresponds to the distance between the clamps in the starting position (Figure 1a), or whether the test-piece is longer (Figure 1b)⁷. Even the shape of the vulcanized groove—deviations in the molding are inevitable—has a significant effect on the results. Various authors⁸ have referred to this cause of great variations in the test results. Our own measurements agree with this.

In our experiments we were very careful to arrange the nature of the stress clearly. Our test-pieces were extended uniformly in the front and the back. The magnitude of the extension could always be given exactly. No grooves were present.

Experiments on tear propagation (tear growth) have been carried out⁹ by several authors with the machines mentioned above. The stressing took place mostly in the manner reproduced in Figure 1. The initial tear was made in two ways. The test-piece was either completely perforated (with a needle or a knife) at the bottom of a groove (Figure 1), and the increase in the length of the tear determined in relationship to the running time¹⁰ or a cut was made across the test-piece, and the depth of the tear was measured after various times by observing the cut from the side of the test-piece¹¹.

Both methods simplify the problem in an inadmissible manner. They cannot give any information about relationships that might possibly exist between the length and the depth of the tear, since either depth or length extends over the whole test-piece even at the beginning. Since the tear is on the inside of a stressed body in almost all applications, the results could only with difficulty be applied to practical situations.

In the present study we give a method (see accompanying sketch A) with which, for the first time, the length and depth of the tear are measured at the beginning and after various times of stressing. This provides an opportunity to evaluate the tear behavior of elastomers, and, at the same time, to obtain definite information on structural questions with high polymers.



Sketch A.—Anfangsriss signifies the initial cut, Probe the test-specimen, and Kraft the stress.

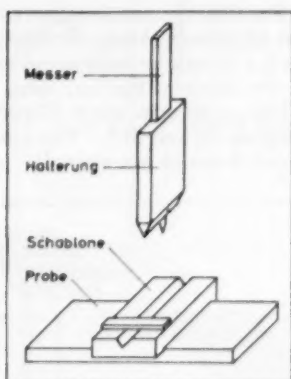


FIG. 2.—Cutting apparatus. Glossary—Messer: knife; Halterung: mounting; Schablone: template; Probe: test-piece.

II. EXPERIMENTAL PROCEDURE

We choose the following dimensions for the test-pieces: length 120 mm., width 25 mm., thickness 6 mm. Figure 2 shows the jig with which we made the initial cut in almost all measurements. The knife is equipped with a mounting that fits exactly into the template. The template is devised to avoid, to a large extent, tilting of the knife, and thus makes it possible to obtain the desired initial length.

The initial cut produced in this way can now be measured under the microscope (magnification $40\times$) for length and depth. For this the test-piece is placed on the mechanical stage of the microscope in a suitable mounting instead of on a slide. With the aid of the cross-hairs in the ocular and the vernier scale on the mechanical stage, the length of the tear is measured exactly to 0.1 mm. The following procedure is used for measuring the depth. As can be seen from Figure 3a, one first focuses sharply on the upper edge of the cut (Point A). To focus on the "valley" (Point B)¹² sharply the stage of the microscope must be

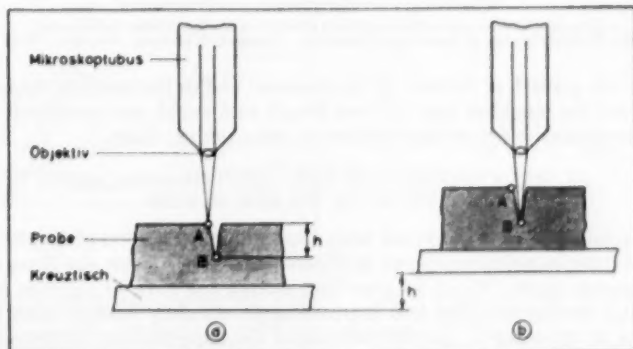


FIG. 3, a and b.—To measure the depth of the tear with a microscope. Glossary—Mikroskoptubus: barrel of microscope; Objektiv: objective; Probe: test-piece; Kreuztisch: stage.

raised by the height h . For this, the coarse adjustment is used. If a suitable scale is fitted to the coarse adjustment knob, the depth of the tear (measured at its deepest point, Figures 3 a-b) can be determined exactly to 0.05 mm.

After the length and the depth of the tear have been measured, the test-piece is mounted in two clamps 80 mm. apart (Figure 4a). Then the piece is periodically extended (Figures 4b and 5)¹². The number of strokes is 250 per minute (frequency of about 4 cycles per second). At specific time intervals

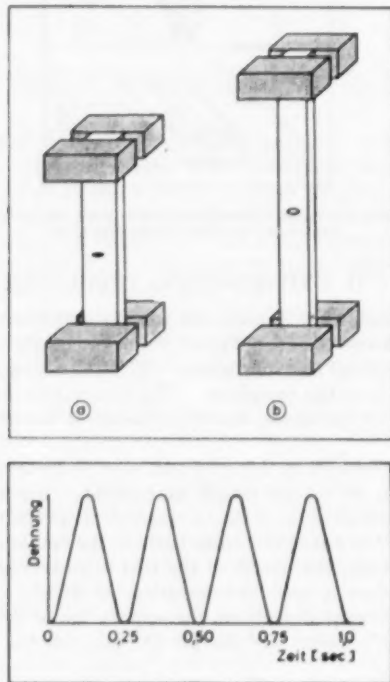


FIG. 4, a and b.—Apparatus for the extension of the test-pieces (schematic).
FIG. 5.—Periodic change of the extension applied. Glossary—Dehnung: extension; Zeit: time.

suited to the growth of the tear in the material and to the tension, the sample is taken from the machine, and the new length and depth are measured.

All investigations were carried out at room temperature.

III. RELATIONSHIP OF THE LENGTH AND DEPTH OF THE TEAR TO THE STRESS

The relationships that appear with a maximum extension of 50 per cent for natural rubber samples are shown in Figures 6a and b. From the three series of measurements given, it can be seen that during the first 60 minutes both the length and the depth of the tear increase approximately linearly with the running time of stressing¹⁴. As the position of the experimental measured points show, the deviations are only very small. (The measured points show only a small scattering.)

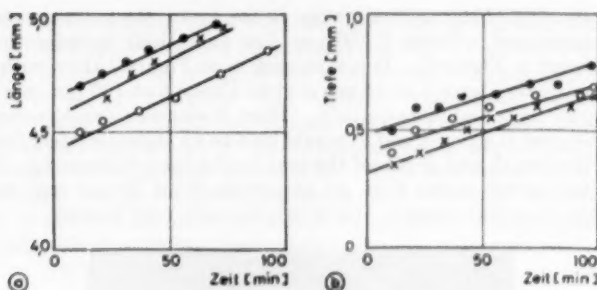


FIG. 6. a and b.—Length and depth of tear in relationship to time in dynamic stress. Frequency: 4 cycles per second; maximum extension: 80%; natural-rubber vulcanizate. Glossary—Länge: length; Zeit: time; Tiefe: depth.

Now the first question to come to mind is what effect various stresses exert on the growth of the tear. For this purpose we have subjected our test pieces to extensions of 25 to 125 per cent. The results are summarized in Figure 7. The individual curves represent mean values of 4 to 8 measurements in each

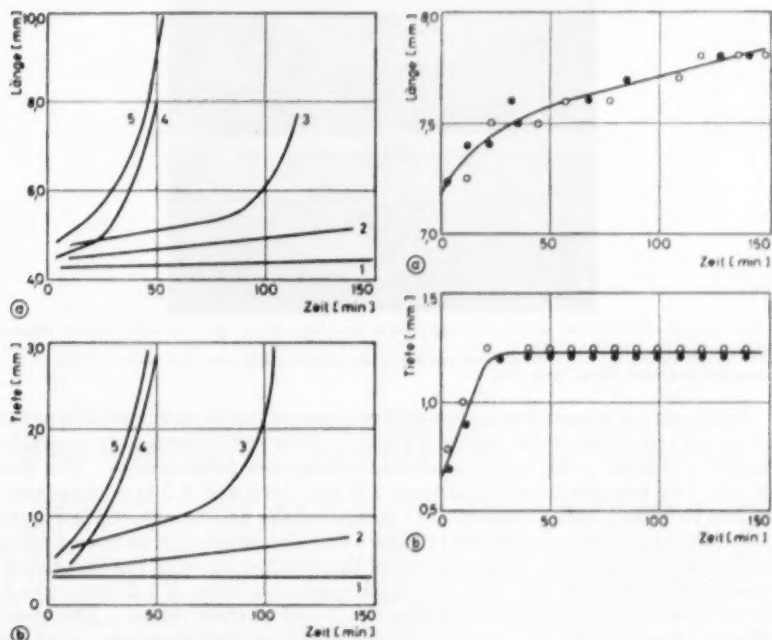


FIG. 7. a and b (left).—Length and depth of tear in relationship to time. Test piece dynamically stressed. Frequency: 4 cycles per second; curves 1, 2, 3, 4 and 5 measured at 25, 50, 100, 110, and 125% of maximum extension; curves averaged.

Länge: length; Tiefe: depth; Zeit: time.

FIG. 8. a and b.—Tear with greater initial length and depth than in Figure 6. Test-piece dynamically stressed.

Länge: length; Tiefe: depth; Zeit: time.

instance. Because of the approximation to the mean, the experimental points were not reproduced. Curve 2 (50 per cent extension) includes the results already reported in Figure 6. It can be seen from Figure 7 that, with increasing extension (from Curve 1 at 25 per cent to Curve 5 at 125 per cent), length and depth grow more and more quickly. Here, it seems as if small extensions of 25 and 50 per cent (Curves 1 and 2) would lead to an approximately linear relationship of the length and depth of the tear to the time of stressing. Furthermore, a rough survey shows that, on exceeding about 50 per cent maximum extension, the growths in length and depth increase very sharply.

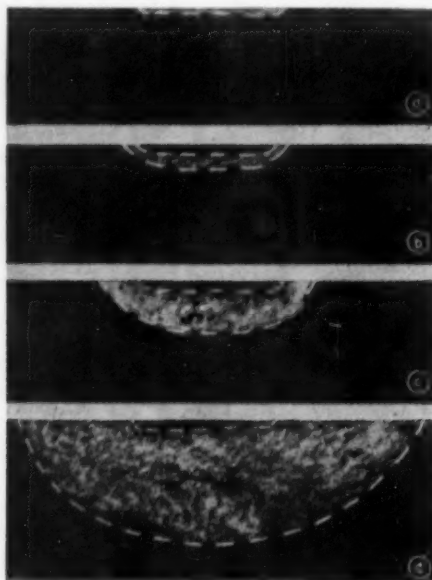


FIG. 9. a-d.—Photographs of cuts in test-pieces in the plane of the tear, carried out after various periods of stress. Running times: a) 0 min.; b) 20 min.; c) 38 min.; d) 41 min.; maximum extension: 125% (magnification 4-1 \times). Border lines, surface of the break; initial tear and surface of the break; undamaged test-piece shown by broken line.

In the results reported so far we always chose about the same initial lengths (about 4.5 mm.) and depths (about 0.4 mm.). It is now important to ascertain whether a change in the initial conditions creates new relationships. For this purpose, two samples with initial tears 7.2 mm. long and 0.7 mm. deep were stressed to 50 per cent extension. We compared the findings, shown in Figure 8, with the known case illustrated in Figure 6. The length now increased more slowly than in Figure 6. The behavior of the depth of the tear was surprising. Already after about 30 minutes, the depth reached a value of 1.2 mm., which did not show any further change during the period of observation. The great difference found here, compared with our previous measurements, must be explained below.

IV. RELATIONSHIP BETWEEN LENGTH AND DEPTH OF TEAR

The results in Figure 8 make it clear that the growth of the tear depends very much on the dimensions of the tear (length and depth). Nor is it surprising that a long tear behaves differently from a short one.

In order to investigate these relationships in greater detail, we cut right through various test-pieces along the plane of the tear. Figures 9a-d reproduce photographs of test-pieces taken at the same stress (125 per cent extension) after 0, 20, 38, and 41 minutes. The "surfaces of the break" can be clearly recognized. In all the cuts not reproduced here, they also have a semi-elliptical form. On closer observation of the otherwise crude semi-ellipse, a narrow smooth area can be recognized at the brim. This part comes from the initial cut by the knife. It should also be mentioned that the depth of the tear, which can easily be determined after the sample is cut open, always agreed exactly with the one we had calculated beforehand.

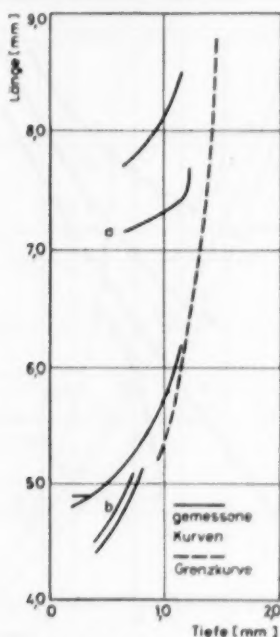


FIG. 10.—Length-depth diagram at 50% of maximum extension.
a taken from Figure 8, b from Figure 7 or Figure 6.

gemeinsame Kurven: measured curves. Grenzkurve: limiting curve. Länge: length; Tiefe: depth.

One could now assume that the fracture surfaces always appear as semi-ellipses, with a fixed ratio between the major and minor semi-axis (here half the length to the depth of the tear). It was, therefore, a question of investigating the previous results to see whether such a fixed ratio of length to depth of tear could be recognized. For this purpose, a series of measurements, all of which were carried out at 50 per cent extension, is summarized in Figure 10. Since we are dealing partly with average value curves, we have again not entered the experimental or data points. The curve designated as *a* corresponds to Figure 8. In curve *b* we again find Curve 2 of Figure 7 (or Figure 6). In Figure 10 we have therefore compiled a series of measurements of test-pieces subjected to equal stresses, but with varying initial tears. As the figure shows, all the curves flow into a limiting curve, which we have indicated by the broken line. In most cases with arbitrarily chosen initial conditions, the values will,

at first, fall outside this limiting curve. With stressing, however, length and depth will grow in such a way that they run into the limiting curve.

We wanted to obtain further information on the limiting curve. In Figure 10, our measured curves always began to the left of the limiting curve. The initial length of our cuts was always greater than the "right" ratio of length to depth, which exists only on the limiting curve. In Figure 11 we have plotted, in addition, measurements with a greater initial depth (Curve 3). The curve designated by D is about identical with the limiting curve. All the other curves flow into it. The connection is seen very well here. If the initial length is too great (Curves 1 and 2), the length at first grows more slowly than the depth. In the length-depth diagram, therefore, the curves are concave up-

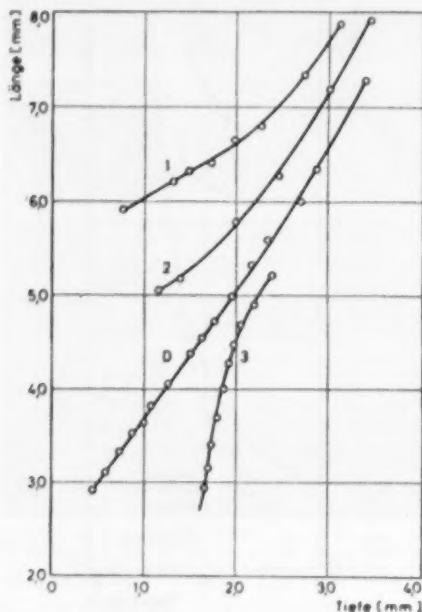


FIG. 11.—To explain limiting curve D. Curves 1 and 2, with too large an initial length, and curve 3, with too small an initial length, run into limiting curve D in the course of the stress.
Länge: length; Tiefe: depth.

wards. If the initial depth is too great (Curve 3), the depth at first grows more slowly than the length. Curve 3 is, therefore, concave downwards. These measurements serve to show that it is not difficult to determine the limiting curve.¹⁵

Now it must be determined whether the position of the limiting curve changes with the stress. In Figure 12 are plotted the results of investigations with a 50 per cent extension (A), a 100 per cent extension (B), and a 110 per cent extension (C) for the same natural rubber compound. The curves shown coincide approximately with the limiting curves, as can be seen from other measurements that have not been reported. Curve A is already familiar from Figure 10. It is evident from Figure 12 that, with increasing extension, the

slope of the limiting curve diminishes. The position of the limiting curve, therefore, depends on the stress.

In Figure 12 the time is plotted as the number of minutes which elapse before the point in question (in the length-depth diagram) is reached. This presentation is intended only as a rough survey for the time being. But the following is already clear: to get from 5 to 6 mm. in length of tear, 500 minutes elapse at 50 per cent extension, 20 minutes at 100 per cent extension, and 10 minutes at 110 per cent extension. Various periods of times are required to traverse the limiting curve, according to the extension applied.

In the measurements in Figure 12, the same compound was subjected to various extensions. In Figure 13 we have retained the 50 per cent extension,

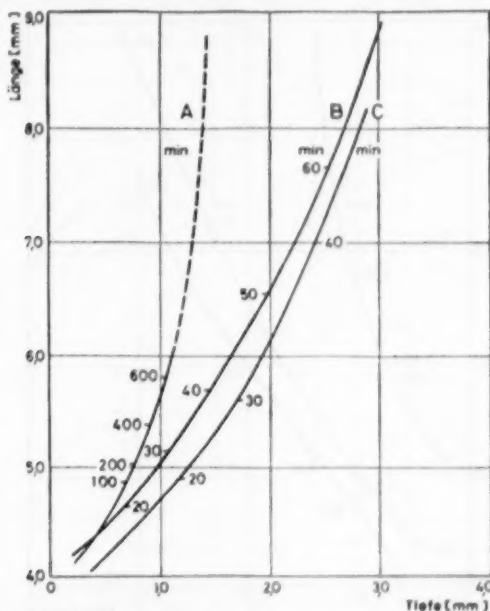


FIG. 12 (right).—Limiting curves of a natural rubber of Quality NK. Curves A, B and C are measured at 50, 100, and 110% of maximum extension; figures indicate time elapsed in minutes.

Länge: length; Tiefe: depth.

but changed the compounds. Curves A and D were determined for two compounds of natural rubber (NK), curve V for Vulkollan (a trademark for elastomers based on polyester isocyanate addition). The measurements show that the position of the limiting curve is also strongly dependent on the compound.

We wish to summarize these results as follows: In the course of the stressing, a ratio of length of tear to depth of tear is set up that is represented by the limiting curve. However, the position of the limiting curve on the length-depth plot depends on the magnitude of the stress and the compound¹⁶.

V. RATE OF TEAR

All our previous investigations were aimed at being able to make binding statements on the growth of tear. In Figure 7 we gave a summary of a series

of measurements. The results of Figure 8, however, could not be explained by this. The problem was thus not yet solved. Yet, the investigations described in Section IV have explained the relationship of length and depth of tear. There is a limiting curve, dependent on material and stress, into which all our curves in the length-depth diagram run, without regard to the initial measurements. In order to get away from the initial dimensions of a tear, one must always try, in evaluating these factors, to stay in the neighborhood of the limiting curve.

The question now arises as to what quantity is suitable for the classification of a compound according to its tear behavior. If we look at Figure 7 again, we see that, with varying extension, the slope of the curves in the length-time and

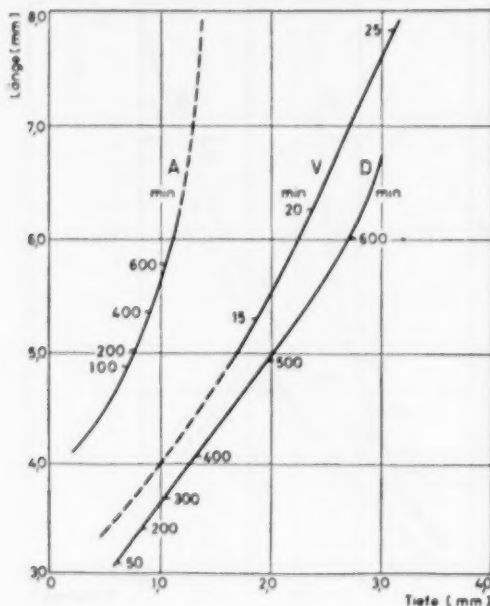


FIG. 13.—Limiting curves at 50% extension. A and D measured for natural rubber, V for Vulkollan—Länge: length; Tiefe: depth.

depth-time diagram changes. The slope obviously offers the correct quantity. It has the dimension length/time, i.e., that of velocity. Let us introduce the designation *rate of tear* for this, and—in order to use convenient numbers—let us measure it in μ/min . The rate of tear is a very clear quantity. At higher rate values, a tear grows more quickly than at low ones.

The rate of tear as a measure for the cut growth (tear propagation) must be determined close to the appropriate limiting curve, as we explained at the beginning of this paragraph. But a further factor involved here must be considered. Even on the limiting curve, the rate of tear is not constant. Instead, the rate generally increases with increasing length of tear (and also with depth), as can be seen from the times given in Figures 12 and 13. We must, therefore, consider two things in the evaluation of the material. First, only measurements

near to the limiting curve appropriate to the material and the stress may be used. Secondly, the length of the tear at which the rate of tear is calculated must always be indicated.

The introduction of the rate of tear puts us in the position to compare different materials under variable stress. Such a comparison is given in Figures 14a and b. Here the individual values were obtained, as has already been mentioned, from the slopes of the curves (that is, through differentiation) in the length-time and depth-time diagram (e.g., Figures 6, 7, and 8). In Figure 14b it seemed more suitable to show the rate of tear, not as dependent on the depth of tear, but as dependent on the length of tear. The letters and indexes are explained in the caption. We had to use a logarithmic scale for the ordinates in order to be able to present a large range clearly. The great difference between

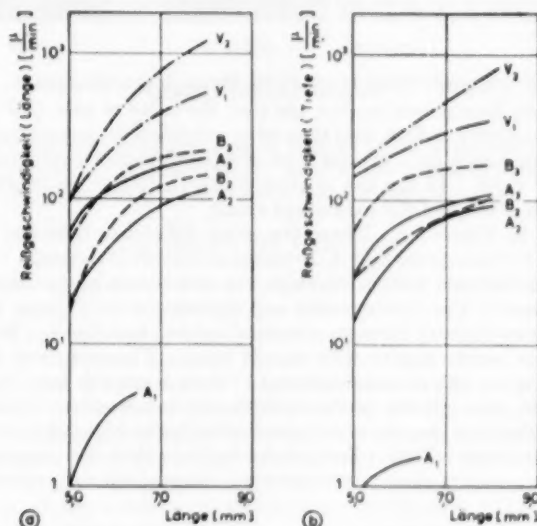


FIG. 14. a and b.—Rate of tear in relation to length of tear. A and B measured for natural rubber, V for Vulkollan; indices 1, 2 and 3 indicate 50, 100, and 125% of maximum extension. Glossary—Reißgeschwindigkeit: rate of tear; Länge: length; Tiefe: depth.

natural rubber and Vulkollan in the figure is striking. The rate of tear for the Vulkollan (V) investigated here is greater by one or two orders of magnitude, depending on the extension, than for natural rubber (A, B)¹⁷.

It would now be rewarding to know the relationship of the rate of tear to the extension. Exact knowledge of such a relationship, of course, requires very many measurements. First of all, investigations with small extensions are very time-consuming. Thus for the measurement of the natural-rubber compound A, for example, at 50 per cent extension (A_1), about 14 hours of running time was necessary (see Curve A, Figures 12 and 13). This could, of course, be shortened by increasing the speed of the machine and by changing the temperature of the test. These points will be taken up again in Section VII.

In Figure 15 we merely wish to indicate how the rate of tear depends on the stress. From Figure 13 we take the rates at extensions of 50, 100, and 125 per cent for compound A of natural rubber with a length of tear of 6.5 mm. Natu-

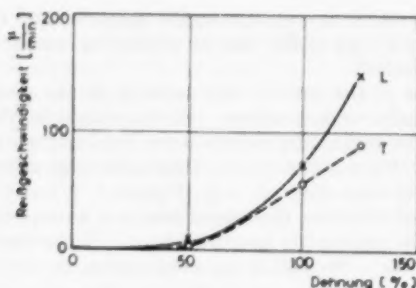


FIG. 15.—Relationship of rate of tear and extension in natural rubber of Quality A. Length of tear: 6.5 mm. L: rate of tear for length; T: rate of tear for depth. Glossary—Reißgeschwindigkeit: rate of tear; Dehnung: extension.

rally, the curve in Figure 15 must also pass through the zero point. From the position of these four points we can see that the rates of tear (for length and depth) increase slowly at first, and then very quickly with increasing extension. This result, found here for a special type of natural-rubber compound, is probably generally valid. In the use of elastomers, therefore, an effort should be made, if possible, to keep the extensions small.

We return to Figure 14. There the great difference between the curves designated by V (Vulkollan) and A, B (natural rubber) is striking. In order to investigate this further, we cut through our test-pieces perpendicular to the plane of the tear. The photographs are reproduced in Figures 16a and b. Figure 16a shows the cut through a natural rubber test-piece. We recognize the effort of the tear to ramify (low rate of tear). The picture of a Vulkollan test-piece in Figure 16b is quite different. Here a smooth tear (high rate of tear) goes right through the piece without any ramification. Certainly the nature of the fillers and the degree of cross-linking in the high polymer determine the course of the tear. Both photographs indicate that the magnitude of the rate of tear in various materials is decisively influenced by their structure.

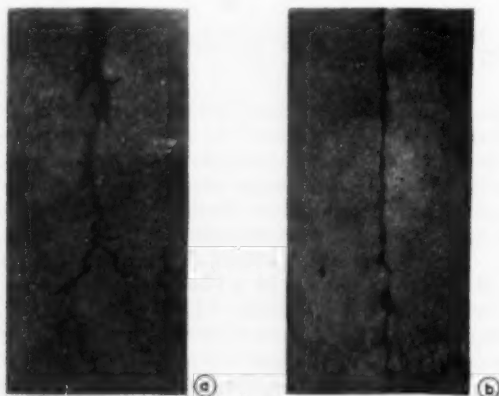


FIG. 16, a and b.—Photographs of stressed test-pieces, cut through perpendicularly to the plane of the tear. a shows an NK test-piece; b a Vulkollan test-piece (magnification 10 X).

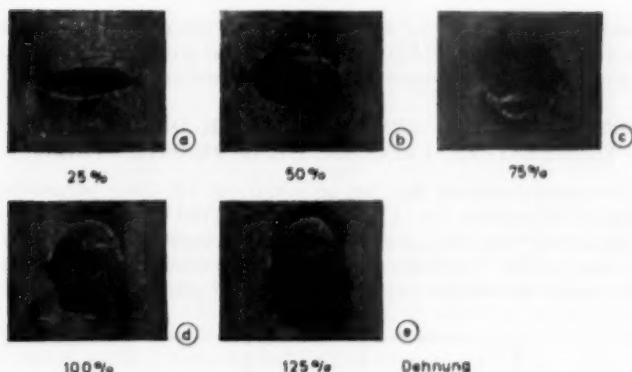


FIG. 17, a-e.—The gaping of a tear (width of tear) with increasing extension.
Glossary—Dehnung: extension.

With the introduction of the rate of tear as a characteristic quantity, we have already reached one definite goal. Now in the following sections we shall report a few more observations that seem noteworthy to us.

VI. WIDTH OF THE TEAR

In the foregoing sections we have reported in detail the behavior of length and depth of tear. Taken precisely, however, a tear is a three-dimensional problem. One can only speak of a measurable width of tear when the damaged piece is extended (the tear gapes). Figures 17a-e show such a test-piece that was elongated up to 125 per cent. The proportions are also shown graphically in Figure 18. With small extensions the width is smaller than the length, at about 75 per cent it becomes equal in size (circular shape), and with even longer extensions exceeds the length. Besides, in Figure 18 the depth of the tear is noted, which, just like the length, decreases with the extension.

Here the depth was determined with a probe (see Section VIII), a departure from our usual procedure.

A knowledge of the width of the tear does not contribute anything new for the investigations within the framework of the research here reported. It is necessary to know it, however, if calculations of the forces appearing at indi-

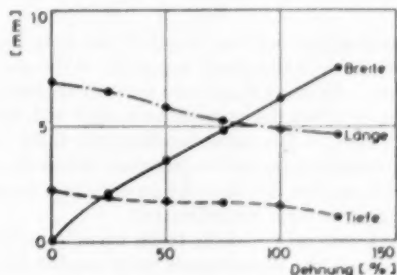


FIG. 18.—Length, depth, and width of the tear photographed in Figure 17 in relationship to the extension.
Glossary—Breite: breadth; Länge: length; Tiefe: depth; Dehnung: extension.

vidual points on the tear are set up on the basis of the geometric relationships. Furthermore, one could always give the width instead of the length or depth of the tear, since these three magnitudes are dependent on each other.

VII. OBSERVATIONS AND REMARKS ON THE DIRECTION OF TEAR, TEMPERATURE, FREQUENCY AND TENSILE STRESS

In all the cases discussed thus far, an initial cut was made perpendicular to the direction of the tension (i.e., **I**). Then we observed the continuation of such a tear. Departing from this, an experiment is represented in Figure 19a and b, in which a tear parallel (**II**) to the direction of the tension is also observed. The great difference in the tear propagation of both test-pieces can be seen from the

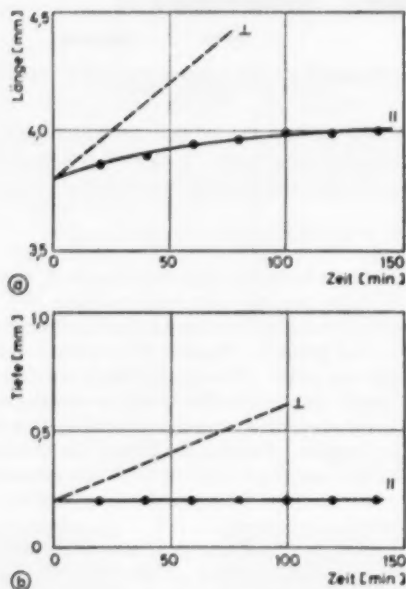


FIG. 19, a and b.—Tear perpendicular (**I**) and parallel (**II**) to the direction of tension. Glossary—Länge: length; Tiefe: depth; Zeit: time.

figure. At 100 per cent extension the length grows only imperceptibly within the period of observations, and the depth not at all, if the tear lies parallel to the direction of the tension. In tears that have various angles of inclination to the direction of stress, the one that lies perpendicularly¹⁸ will, therefore, grow most quickly. The finding that, in the usual bending tear tests (no initial tear), the tears always appear perpendicular to the direction of the stress agrees with this. In Section I we pointed out the fact that it can only be a question of the growth of microscopic or submicroscopic irregularities.

With regard to the temperature of the tests, we only noted in the description of the experiments that all the experiments were carried out at room temperature. Naturally, the temperature of the environment of the test-piece is meant by this. There are various studies that report on the growth in relationship to

TEMPERATURES IN THE INTERIOR OF TEST-PIECES
UNDER DYNAMIC STRESS

Extension (%)	Temperature ($^{\circ}$ C) at thickness of test-piece	
	6 mm.	9 mm.
25	43	—
50	58	—
100	70	85
110	75	90
125	80	—

the temperature of the environment¹⁹. For the time being we have not carried out such experiments. However, we want to indicate the temperature (at equilibrium) that occurs in the interior of the test-pieces under dynamic stress. It is obvious that the temperature in the interior of the test-pieces rises with increasing extension. The values, measured with a thermocouple, can be seen from the table.

In addition to the increase in temperature with increasing extension, a comparison of the second and third columns of the table shows that a higher temperature develops with a 9 mm. thick test-piece than with a piece 6 mm. thick. This result is easy to understand. With the 9 mm. sample, more heat is produced as a result of the 50 per cent greater volume. Since, with a 50 per cent increase of the thickness of the test-piece, the surface is enlarged only inconsequentially, radiation remains almost unchanged. We have found no statement of the temperature in the interior of the test-pieces in earlier studies. It seems important to us, however, to point out that the temperature of the environment and the temperature of the interior of the test-piece are determining factors for the growth of the tear (thus for the rate of tear). Both together would give us the temperature in the immediate environment of the tear, but this temperature can be exactly measured only with difficulty.

All our measurements were carried out at a frequency of 4 cycles per second. It would naturally be desirable to reexamine what effects the frequency of the machine had on the results of measurement. We can hardly believe that such an effect does not exist²⁰. According to our measurements of the temperature in the interior of the test-piece, as reported here, the conclusion would have to

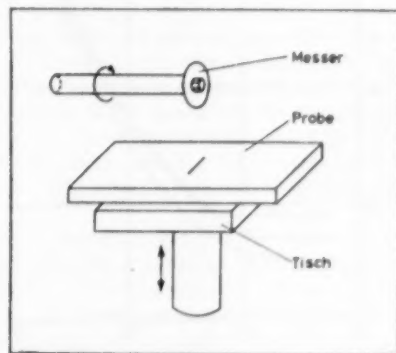


FIG. 20.—Cutting apparatus. Glossary—Messer: knife; Probe: test-piece; Tisch: table.

be reached that an increase of the frequency produces an increase of the temperature and, with it, a change in the rate of tear.

Until now we have always spoken only of the extension to which the test-pieces were subjected. That was because the extension can be measured with particular ease and precision. Perhaps it would be more satisfactory to indi-

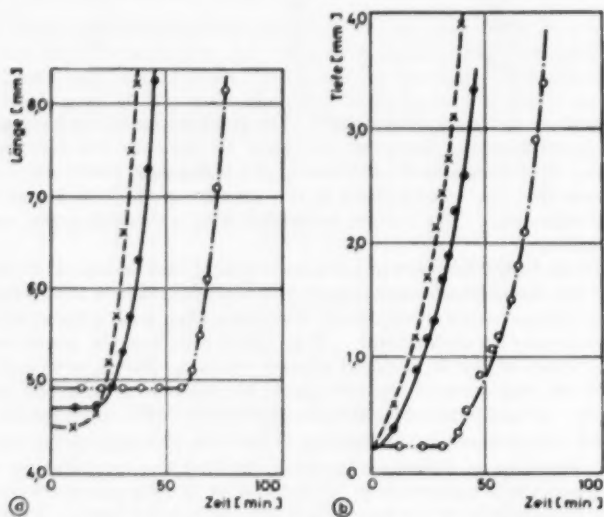


FIG. 21, a and b.—Length and depth of tear in relationship to period of stress.

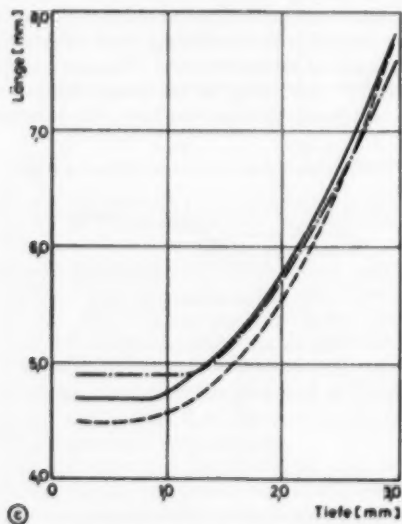


FIG. 21 c.—Length-depth diagram.

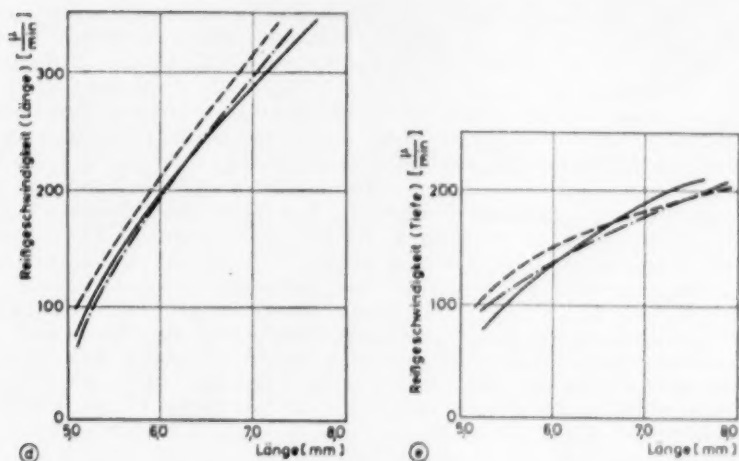


FIG. 21. d and e.—Rate of tear in relationship to length of tear. Glossary—Länge: length; Tiefe: depth; Zeit: time; Reißgeschwindigkeit: rate of tear.

FIG. 21 a-e.—Summary of the five curves required for the evaluation of tear, shown for Vulkollan.

cate, instead, the tensile stress used. Unfortunately the determination of the tensile stress is not a very simple matter. If an elastomeric test-piece is extended, the force required for the extension changes in the course of the period of observation. Here relaxation processes are involved. For this reason we should like to omit giving the E modulus, which can be determined from the tensile stress and extension, although we have always carefully measured force and cross-section of the test-piece (even in the stressed state).

VIII. DETAILS FOR CARRYING OUT THE TEAR TEST

As a supplement to what has been said in the above sections, we now wish to make a few more statements on the testing process.

There are many studies on the influence of the form of the knife or needle²¹. The following can be said in this connection. Figure 9 shows photographs of various cuts. Under close observation, the smooth surface of the cut contrasts clearly with the rough surface of the break (due to tear propagation) in every cut. A transition takes place from the stage indicated by the initial tear to the region of the granular surface of the break. These surfaces of the break grow in the form of semi-ellipses. Their further growth then no longer depends on the initial damage.

We were able to make these findings from the observation of the section of the tears. We have, however, also provided the initial cut with the arrangement sketched in Figure 20. Here the test-piece is clamped to a table that can be run under the knife. The damage can now be caused quickly and with specific definition. Even with this apparatus the same values for the rate of tear were found as with the apparatus described in Figure 2.

As we stated in Section II, the dimensions of the clamped piece were $80 \times$

25 × 6 mm. We have naturally investigated other sizes for the same free length of specimen between the clamps. The aim must be to choose the dimensions so that the rate of tear will be independent of the form of the test piece. This condition is certainly fulfilled if the length of the tear formed is small, compared with the specimen width and the depth is small compared with its thickness. Our investigations show that an increase in the width of the test-piece from 25 to 45 mm. does not entail any change of the rate of tear. In the cases observed by us (the length of the tear was observed only to 9 mm. at the most), a width of 25 mm. is sufficient. It is more difficult to make statements about the proper thickness of the test-piece. Since we have shown depths of tear of up to about 3 mm., one would assume that a change of the thickness of the test-piece from 6 to 9 mm. causes a reduction of the rate of tear. A glance at the table shown above, however, shows that an increase of the thickness of the test-piece leads to an increase of temperature. In general, an increase of temperature in natural rubber involves an increase of the growth of the tear²². Thus our measurements of the 9 mm.-thick tear piece show a higher rate of tear. It seems to us better to increase the thickness of the test-piece to 9 mm. If the tears are then allowed to become 3 mm. deep, only one-third of the total test-piece thickness is reached.

In connection with Figure 1 we reported on the influence of the free length of the specimen between the clamps (*g*). In our experimental arrangement (Figure 4), the strip is clamped without any bend. Nevertheless, it is inevitable, with the "plastic extension" in elastomers, that there should be an elongation of the test-piece during the stressing. When the test-piece returns to the initial position, it shows a slight bend (as in Figure 1b). We have investigated this influence more closely. For this purpose, one test-piece was removed and measured after 1 minute of testing, while the other remained in the machine for 15 minutes before it was removed. For the same total consecutive time under the same conditions, a test-piece which has been frequently removed does indeed show a somewhat higher rate of tear (a small difference in the maximum extension). The influence on the result is not significant, however, and can be disregarded.

For almost all the measurements discussed in the present study (with the exception of those given in Figure 18), the depth of the tear was determined with the microscope according to the method shown in Figure 3. This procedure was very well suited for our test strips. It becomes difficult, however, when the depth of the tear has to be determined on the finished article, e.g., on the tire. In order to indicate the depth of tear for such applications too, we devised a "depth probe". A dial gauge makes it possible to read off the travel of the probe (AB in Figure 3), which is under constant pressure from a spring. By blank measurements near the tear, the penetration of the probe into an undamaged neighboring surface is observed. This distance is deducted in the measurement. With this apparatus we were successful in obtaining very good agreement with the microscopic measurement.

The growth of tear is certainly affected in some manner by the period of storage of the material. We have not investigated this relationship in detail. But in testing the natural-rubber samples, we began at least 48 hours after vulcanization.

In conclusion, the testing procedure, as exemplified with three Vulkollan test-pieces of the same compound, is discussed²³. In Figure 21, a and b, the length and depth of tear are measured in relation to the period of stress.

While two curves are close together, the one indicated by dots and dashes seems to exhibit a fundamental difference in behavior. This difference has been eliminated in the length-depth diagram (Figure 21c). From a length of 5 mm. and a depth of 1.3 mm., all curves behave very similarly, since they run into the limiting curve. It is now easy to see the cause of the different behavior: the initial length of the three tears was not equal. Figure 21, d and e, is then calculated by differentiation from the curves of Figure 21, a and b. It is expedient here to keep to the vicinity of the limiting curve from the beginning. We have now obtained the rate of tear as a suitable parameter for evaluating the continued growth of the tear in its dependence on the length (and also the depth according to Figure 21c). All three Vulkollan test-pieces agree very well in their rates of tear, as Figure 21, d and e, show.

IX. PROSPECTS

In the various sections of this paper we have reported on the behavior of tear as evidenced by our measurements, which are readily reproducible. The rate of tear was introduced as a suitable parameter for evaluation purposes. With this it becomes possible to undertake reliable routine tests²⁴.

The possibilities offered, however, are by no means exhausted with the description of the test procedure. With the knowledge of a usable method of investigation, one will now be on the search for relationships. Relationships must exist between rate of tear and other magnitudes that can be determined for elastomers.

Purely qualitative relationships have already been ascertained with ease. Thus we are able to understand from the pictures shown in Figure 16 that the ramification of the tear caused by the structure of the high polymer must lead to a low rate of tear. A change of filler affects the results of measurement very strongly. For example, the position of limiting curves A and D in Figure 13 and the rate of tear reflected by both curves is caused only by the variation of the nature of the filler in otherwise unchanged vulcanizates.

But we would also like to arrive at quantitative conclusions. First of all, it is in order to search for a relationship between the rate of tear and the E modulus. In Section 7 we have already discussed the difficulties in the way of an exact determination of the E modulus. From our investigations to date, however, it is certain that the position of the limiting curve and the magnitude of the rate of tear depend on the E modulus. Exact statements are not yet in order. It must be the task of later investigations to produce information on such relationships.

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- ¹ Summary in Buist and Williams, *India Rubber World* **124**, 390, 447, 567 (1951).
- ² ASTM-D430-51T; ASTM D813-52T.
- ³ British Standards 903, Pt. 26.
- ⁴ ASTM D430-51T; British Standards 903, Pt. 26; *Rubber Age* (N. Y.) **26**, 542 (1930).
- ⁵ The presence of a groove creates an area of particularly high stress in the test-piece. Here the first tears appear (beginning of tear) when the strip is stressed without previous damage.
- ⁶ In tests it is customary to indicate only the length of the stroke.
- ⁷ Buist²⁵ finds that, in the results, deviations by a factor of 100 arise because of this.
- ⁸ Newton and Scott, *J. Rubber Res.* **16**, 245 (1947); Buist and Williams, *Trans. Inst. Rubber Ind.* **27**, 209 (1951).
- ⁹ Holt and Knox (*Rubber Age* **60**, 689 (1947)), in a summary of various procedures, point to the fact that the ratio of the resistance to tear propagation (or life, i.e., until the sample tears through completely) of GR-S to that of natural rubber is 10²:1 by one method and 2:1 by another. The deviations of two orders of magnitude in the individual methods are caused by the completely different nature of the stress and by differences in the form of the test-pieces or cuts.

¹⁰ ASTM D813-52T.

¹¹ Carlton and Reinhold, *India Rubber World* 108, 14 (1943).

¹² In order to observe the point B, the test-piece must, of course, be extended somewhat. The error that thus enters the measurement of depth is unimportant.

¹³ Extension in the length always produces a contraction in the width.

¹⁴ In place of the running time the number of load cycles that have already acted on the test-piece could, naturally, also be indicated. With the knowledge of our frequency of 4 cycles per second, such a conversion can be carried out at any time.

¹⁵ In our presentation, therefore, the sign of the curvature changes on the limiting curve.

¹⁶ The existence of an extreme relationship between the surface of the break defined by the limiting curve and the stress is obvious. But we do not want to go into it within the framework of this study.

¹⁷ We point out the fact that we have carried out a comparison here at 50% and 100% of maximum extension. With small extensions, which appear frequently in practice, the relations may be different.

¹⁸ Present measurements make it seem possible that, in our test-pieces, an angle of 60° to the direction of tension is particularly characterized by a high rate of tear.

¹⁹ Newton and Scott, *J. Rubber Res.* 16, 245 (1947); Holt and Knox, *Rubber Age* (N. Y.) 60, 689 (1947); Buist, *Trans. Inst. Rubber Ind.* 29, 72 (1953); Rainier and Gerke, *Ind. Eng. Chem. Anal. Ed.* 7, 368 (1953).

²⁰ Rainier and Gerke, *Ind. Eng. Chem. Anal. Ed.* 7, 368 (1953).

²¹ Buist and Powell, *Trans. Inst. Rubber Ind.* 27, 49 (1951).

²² Buist, *Trans. Inst. Rubber Ind.* 29, 72 (1953).

²³ The type of Vulkollan measured here is different from the compound V discussed in Figure 14.

²⁴ In routing tests a depth probe (Section 8) will be used in place of the microscope for the determination of the depth of tear.

EXPERIMENTAL EXAMINATION OF THE STATISTICAL THEORY OF RUBBER ELASTICITY. LOW EXTENSION STUDIES *

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INTRODUCTION

As part of a series of experimental investigations designed to provide a critical evaluation of the Guth-James theory of rubber elasticity¹, a careful study of the behavior of two rubbers at low extensions was undertaken. The low extension region was chosen for this initial study because of the interesting behavior of rubbers in this region. As is well known, rubbers exhibit a thermoelastic inversion in the vicinity of 5 to 7 per cent extension. This phenomenon was first observed by Joule² in 1859, while engaged in measuring temperature changes accompanying the adiabatic stretching of rubber. Joule noted a slight cooling at low extensions, followed by a rise in temperature at higher extensions. These observations, along with the thermodynamic analysis of Kelvin³, indicated that, for rubber specimens held at constant extended lengths, the temperature coefficient of stress must be negative at low extensions and positive at higher extensions. The first direct observation of this change of sign of the temperature coefficient of stress was made by Meyer and Ferri⁴ in 1935. This was confirmed by the experimental work of Anthony, Caston, and Guth⁵, and of Peterson, Anthony, and Guth⁶ in 1942. Later experimental work by Wood and Roth⁷, Gee⁸, Treloar⁹, and others contributed much to the understanding of the physical behavior of rubbers. Wood and Roth investigated the effect of working at constant "extension ratio" rather than at constant length, on the stress-temperature relations of rubbers. Gee's early work was concerned primarily with the attainment of better equilibrium conditions through the use of a swelling technique. Treloar investigated deviations from the theoretically predicted stress-strain curve at moderate to high extensions.

All the stress-strain studies mentioned above lacked the precision necessary to test adequately the predictions of the Guth-James theory in the region of low extensions. Accordingly, the present study was undertaken for the specific purpose of testing the theory in this region. The rubbers selected for this study were Butyl (GR-I-18) and Paracril-35. Butyl was chosen because of its relative stability to oxidation in comparison with more highly unsaturated polymers. The GR-I-18 used in this work is an isobutylene-isoprene copolymer having a mole-per cent unsaturation of 1.38. For purposes of comparison and contrast, a second rubber having relatively strong intermolecular forces and a fairly high second-order transition temperature was desired. Paracril-35, a

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copolymer of butadiene and acrylonitrile containing about 35 per cent of the latter, was selected for this purpose. Extensions were limited to the range 0 to 10 per cent for the Butyl rubber, and 0 to 15 per cent for the Paracril rubber. The temperature ranges covered were from -40° to $+40^{\circ}$ C for the Butyl rubber, and from -20° to $+60^{\circ}$ C for the Paracril rubber.

THEORY

The Guth-James theory¹ gives the following expression for the stress as a function of the extension, the temperature, and the pressure:

$$Z = KT \left[L - \frac{V(LTP)}{L^2} \right] \quad (1)$$

Here, $Z = F/A_0$ is the nominal stress, $L = l/l_0$ is the relative length, and $V = v/v_0$ is the relative volume. The quantities A_0 , l_0 , and v_0 are, respectively, the cross-sectional area, the length, and the volume of the unstrained specimen at the reference temperature T_0 . The quantities F , l , and v are, respectively, the tension force, the length, and the volume of the strained specimen at the test temperature, T . P is equal to the hydrostatic pressure of any fluid medium surrounding the specimen, and K is a constant assumed to be independent of both temperature and extension. The factor K , which according to the theory is related to the number of cross-links per cubic centimeter of the rubber, plays the role of an adjustable constant in fitting the theoretical stress-strain curve to its experimental counterpart.

The definitions of Z , L , and V given above are equivalent to normalizing the initial sample dimensions to those of a 1-cm. cube at $T = T_0$. Hence, we may also consider Z to be the total stretching force, and L the actual stretched length in centimeters, for such a model. This interpretation is convenient in the application of thermodynamics to the problem of rubber elasticity. When it is employed, the fundamental quantity of rubber to be considered in thermodynamic equations is then 1 cc., and not 1 gram.

For purposes of resolving the Guth-James force expression or the experimental stress-strain curves into their entropy and internal energy components, the following thermodynamic considerations are useful. Assuming that an equation of state exists for rubber, and that satisfactory equilibrium conditions have been achieved, the combined first and second laws of thermodynamics state:

$$dU = TdS - PdV + ZdL \quad (2)$$

for the case of unilateral extension. Here U is the internal energy, and S is the entropy. Employing the Gibbs function $G = H - TS$, where $H = U + PV$ is the enthalpy, the following stress relation may be deduced:

$$Z = \left(\frac{\partial G}{\partial L} \right)_{TP} = -T \left(\frac{\partial S}{\partial L} \right)_{TP} + \left(\frac{\partial H}{\partial L} \right)_{TP} \quad (3)$$

With the aid of an appropriate Maxwell relation, Equation (3) may also be written in the form:

$$Z = T \left(\frac{\partial Z}{\partial T} \right)_{LP} + \left(\frac{\partial H}{\partial L} \right)_{TP} \quad (3')$$

It is convenient to refer to the first term on the right of Equations (3) and (3') as the entropy component Z_S of the total stress Z and to the second term as the enthalpy component Z_H . Thus:

$$Z_S = -T \left(\frac{\partial S}{\partial L} \right)_{TP} = T \left(\frac{\partial Z}{\partial T} \right)_{LP} \quad (4)$$

and

$$Z_H = \left(\frac{\partial H}{\partial L} \right)_{TP} = Z - Z_S \quad (5)$$

The application of Equations (4) and (5) to the theoretical model represented by Equation (1) yields:

$$Z_S = KT \left[L - \frac{V(LTP)}{L^2} \right] - \frac{KT^2}{L^2} \left(\frac{\partial V}{\partial T} \right)_{LP} \quad (6)$$

and

$$Z_H = \frac{KT^2}{L^2} \left(\frac{\partial V}{\partial T} \right)_{LP} \quad (7)$$

The factor $(\partial V / \partial T)_{LP}$ appearing in Equations (6) and (7) is equal to α_{LP} , where α_{LP} denotes the volume coefficient of thermal expansion of the rubber model, subject to the restrictions of constant length and pressure. For real rubbers the coefficient α_{LP} should be practically indistinguishable from the ordinary coefficient α measured without the restriction of constant length. Evidence that α is nearly independent of extension, for extensions ranging up to 200 per cent, is supplied by the data of Copeland¹⁰. Accordingly, the same behavior is ascribed to the model, and α_{LP} is replaced by α . Further, Poisson's ratio for real rubbers is almost exactly $\frac{1}{2}$, the dependence of V on L and P being practically negligible in comparison with its dependence upon T . Hence, $V(LTP)$ is replaced by $[1 + \alpha(T - T_0)]$ in Equation (6). Equations (6) and (7) thus become:

$$\begin{aligned} Z_S &= KT \left[L - \frac{1 + \alpha(T - T_0)}{L^2} \right] - \frac{KT^2\alpha}{L^2} \\ &= KT \left[L - \frac{1 + \alpha(2T - T_0)}{L^2} \right] \end{aligned} \quad (8)$$

and

$$Z_H = \frac{KT^2\alpha}{L^2} \quad (9)$$

To within the same approximation the original stress, Equation (1), may now be written:

$$Z = Z_S + Z_H = KT \left[L - \frac{1 + \alpha(T - T_0)}{L^2} \right] \quad (10)$$

Equations (8)–(10) are approximate expressions which correspond to the Equations (6), (7), and (1), respectively. They are also exactly the equations which one obtains for the incompressible analog of the original model, i.e., when Poisson's ratio is taken to be exactly one-half. We shall employ Equations (8), (9), and (10) for comparison with experimental results. They are of addi-

tional interest in that they predict two effects which had not been observed in earlier, less precise, experimental work¹¹. First, Equation (10) predicts a non-linear dependence of Z upon T , at constant specimen length. Second, Equation (8) predicts that the thermoelastic inversion extension, i.e., the extension for which $Z_s = 0$, should depend on temperature and, in fact, should increase with increasing temperature, thus:

$$L_{inv} = [1 + \alpha(2T - T_0)]^{\frac{1}{2}} \quad (11)$$

One final point should be noted before proceeding to the experimental part of the work. For a real rubber at atmospheric pressure the enthalpy contribution to the stress, as given by Equation (5), is indistinguishable from an internal energy contribution¹². Thus for all intents and purposes we have $Z_H \simeq Z_U$, or

$$\left(\frac{\partial H}{\partial L}\right)_{TP} \simeq \left(\frac{\partial U}{\partial L}\right)_{TP} \quad (12)$$

EXPERIMENTAL METHOD

The stress relaxation method was selected for obtaining the required equilibrium stress-strain curves. In this method the sample is first extended to a relative length L at the reference temperature T_0 , this temperature being the highest temperature to be used in the experiment. The sample is then held at constant length and at temperature T_0 until the time rate of decay of stress becomes negligibly small, i.e., so small that it can have no appreciable influence on the following stress-temperature run. In the work reported here, the time allotted for this initial relaxation process was usually about 12 to 15 hours. After this stage the temperature is lowered in steps, the length of the specimen still being held constant, and the stress Z is determined at each new temperature after thermal equilibrium has been attained. This procedure is continued until the lowest temperature desired has been reached. Although it is not essential, the temperature may then be raised in steps, and the identical procedure employed for increasing temperatures. Comparison of these data with those obtained for decreasing temperatures affords an excellent check on the degree of reversibility achieved, i.e., on the extent to which undesired time effects have been suppressed. This complete procedure was followed in obtaining all of the results reported here.

By repeating the procedure just described for a series of samples, each sample being stretched to a different extended length, a family of equilibrium stress-temperature curves is obtained. Cross-plotting these for various constant values of the temperature yields the equilibrium stress-strain curves.

The apparatus employed for obtaining the stress-temperature data is shown schematically in Figure 1. The desired temperature within the cylindrical air bath was secured by adjustment of the temperature and rate of flow of the liquid (ethyl alcohol) circulating between the double brass walls of the thermal enclosure. Temperatures were measured with a copper-constantan thermocouple placed near the center of the sample, and were recorded continuously. Dry air (H_2SO_4 -dried) was brought to the required temperature and introduced into the test chamber through the inlet at the base. This provided good mixing in the test chamber, and also prevented the formation of frost around the fused silica rod during low temperature operation. When the system was properly adjusted, temperatures within the air bath could be held constant to within

0.1° C over the complete 80° C temperature range. It was found necessary to include the aluminum strip in order to compensate for changes in length of the supporting iron framework (not shown), which resulted from small changes in room temperature. A Statham strain gauge was used as a null detector, the gauge output being fed to a Brown Electronik recorder. The gauge could be driven up or down by means of the micrometer screw whenever the sample length was to be changed for a new run. During a given run, the gauge was held at a fixed position. When necessary, changes of force detected by it were compensated by changing the weights W in the scale pan suspended from one side of the equal arm beam balance. With a gauge input of 2.4 volts, obtained from a storage battery, a gauge deflection of 1 mil resulted in an output change of 0.32 millivolts. For the 0 to 3 millivolt Brown Recorder employed, this

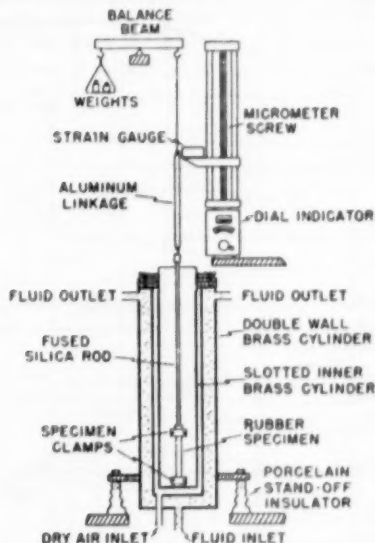


FIG. 1.—Schematic diagram showing main features of apparatus.

corresponded to a deflection of 32 chart divisions. For the same gauge input, the load sensitivity was about 5.8 chart divisions per gram. Brown chart deflections as small as one-half division were easily detectable.

In order to maintain sample lengths constant and independent of temperature, it was necessary that the clamp spacing should remain constant for constant strain gauge output. Conversely, changes in the strain gauge output should accurately reflect changes of the clamp spacing and not be the result of expansions or contractions of some other part of the apparatus. To secure this condition, the inner brass cylinder is threaded at its top end and passes through a threaded cap, which can be firmly fixed to the top of the chamber by bolts and wing nuts. This cylinder is slotted to provide for good air circulation, and has the lower specimen clamp attached to its base. By trial and error the immersion depth of the cylinder was varied until its thermal changes almost exactly compensated those due to the double-walled cylinder, the porcelain insulators,

the clamps, etc. This was done by comparing the thermal expansion of a 4.31-inch strip of copper, mounted between the clamps, with the value to be expected from data reported in the literature¹³. As finally adjusted, agreement to within 3 per cent was obtained over a 90° C temperature range. This represented a discrepancy of only 2×10^{-4} inch from the predicted thermal expansion, and was well within the limits of precision set by the dial-and-screw measuring device. Thus, for rubber samples of lengths 4 inches or greater, extended lengths could be held constant and independent of temperature to better than 0.01 per cent. A second and indirect test of the final adjustment was the use of the apparatus to measure the thermal expansion coefficient of Butyl rubber at zero stress. The linear expansion coefficient obtained was $1.894 \times 10^{-4}/^{\circ}\text{C}$, giving

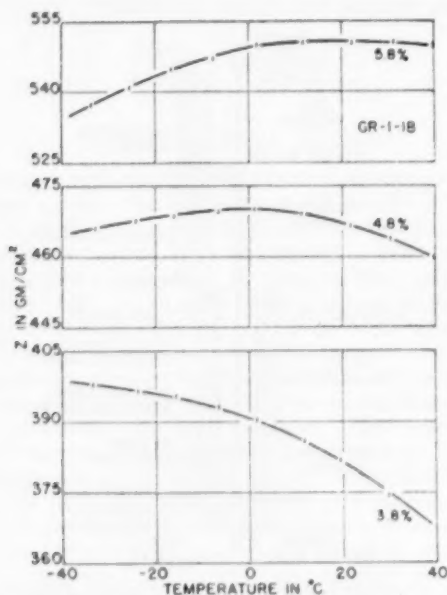


FIG. 2.—Stress-temperature behavior of GR-I-18 for three selected values of percentage extension.

a volume coefficient of $5.68 \times 10^{-4}/^{\circ}\text{C}$. This value compares very favorably with that reported by Bekkedahl¹⁴, namely, $5.67 \times 10^{-4}/^{\circ}\text{C}$ for unvulcanized Butyl, measured with a volume dilatometer. Similar measurements for the Paracril-35 rubber gave a value of $6.65 \times 10^{-4}/^{\circ}\text{C}$ for its volume coefficient of thermal expansion.

The rubber specimens used in this study were died out of standard 6-inch square tensile sheets. The specimen shape was that of a square-headed dumb-bell, previous tests having shown that this type of sample gave excellent correlation between percentage extensions computed from clamp separations and those computed from separation of dots placed on the central part of the specimen. The average dimensions of the neck of the specimen when unstrained were 4 by 0.25 by 0.075 inch.

The rubbers had the following compositions and cures (amounts given in parts by weight):

Butyl rubber		Paracril rubber	
GR-I-18	100	Paracril-35	100
Zinc oxide	5	Zinc oxide	5
Sulfur	0.8	Stearic acid	1
Tetramethylthiuram disulfide	1	Sulfur	1.75
		Benzothiazolyl disulfide	2
Cured 75 minutes at 300° F		Cured 80 minutes at 287° F	

RESULTS

Figure 2 shows the dependence of stress on temperature observed for the Butyl rubber at three different values of the percentage extension. [The percentage extension, as used in this paper, is defined as $100(L-1)$.] Both

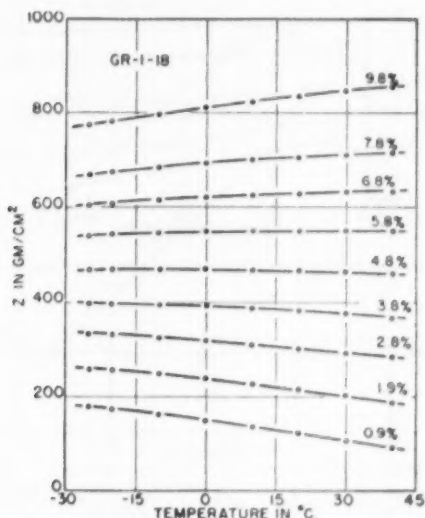


FIG. 3.—Family of stress-temperature curves for GR-I-18.

effects predicted by the theory are confirmed by the curves shown here; the dependence of stress on temperature is decidedly nonlinear, and the thermoelastic inversion temperature is shifted to higher values at higher extensions. Note the shift of the peak to the right as the extension is increased. This is the first time either of these two effects have been observed with certainty in this laboratory. Appreciable deviations from linearity were not apparent in earlier stress-temperature data¹¹, owing both to a lack of sufficient precision in the measurements, and probably also to our failure to maintain extended lengths sufficiently constant during the stress-temperature runs. Curves similar to those shown in Figure 2 were observed also for the Paracril rubber. The complete set of stress-temperature curves is shown in Figure 3 for the Butyl rubber, and in Figure 4 for the Paracril rubber. In order to cover the full range of extensions for each rubber in a single figure, the stress scales used in Figures 3

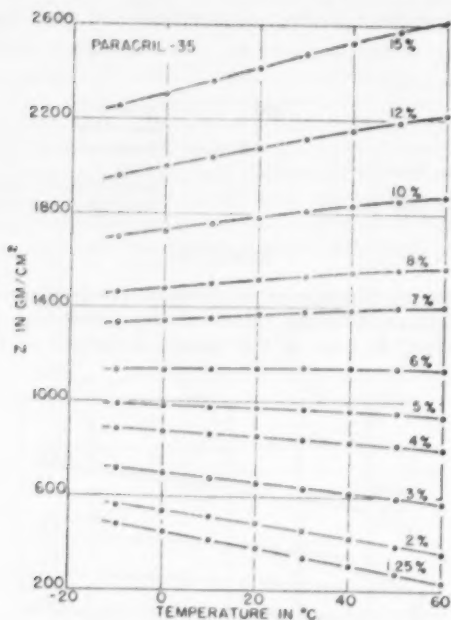


FIG. 4.—Family of stress-temperature curves for Paracril-35.

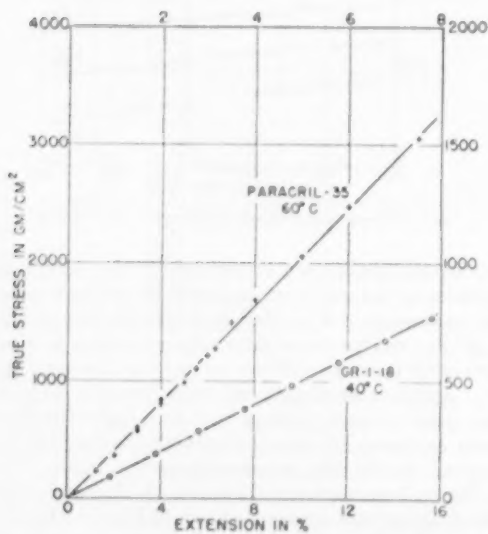


FIG. 5.—"True stress"-strain curves. Use scales along top and right-hand margins for GR-I-18. Scales along bottom and left hand margins are for Paracril-35.

and 4 have been considerably reduced over that employed in Figure 2, with the result that deviations from linearity are now scarcely perceptible.

To evaluate the constant K appearing in the Guth-James theory, the "true stress" was plotted as a function of extension, at the reference temperature T_0 , for each rubber. The required values of Z and L were obtained from the curves of Figures 3 and 4 by cross-plotting. The true stress is defined as the tension force divided by the actual cross-sectional area (not the unstrained cross-sectional area). Making the assumption that Poisson's ratio is exactly 0.5 here, the true stress is then simply equal to the product of the nominal stress Z by the relative length L . This method of plotting yields a linear stress-strain curve at low extensions, as shown in Figure 5. This enables a good determination of Young's modulus, E_0 , to be made in the limit of $L = 1$ and $T = T_0$.

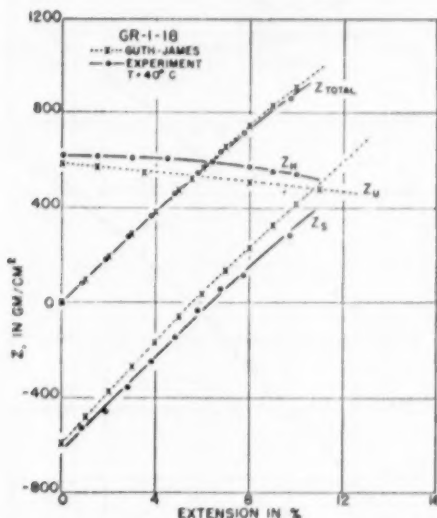


FIG. 6.—Theory vs. experiment for GR-I-18 at 40° C, showing the total stress Z , the enthalpy component $Z_H \approx Z_U$, and the entropy component Z_S as functions of the percentage extension.

The values of E_0 obtained from the curves in Figure 5 were 9.96×10^3 g. per sq. cm. at 40° C for Butyl rubber, and 20.4×10^3 g. per sq. cm. at 60° C for Paracril rubber. These values of E_0 were then equated to the theoretical expression, $3KT_0$, obtained from Equation 10 by differentiating with respect to L and putting $L = 1$ and $T = T_0$. The values of K so obtained were 10.6 and 20.4 g. per sq. cm. \times ° K for the Butyl and Paracril rubbers, respectively. All fitting of theory to experiment in this work was confined to the valuation of K , as just described.

The equilibrium stress-strain curves were obtained from the stress-temperature curves of Figures 3 and 4 by cross-plotting at various fixed values of the temperature. The experimental entropy components were obtained by evaluating the point slope, $(\partial Z/\partial T)_{LP}$, as a function of temperature for each of the stress-temperature curves. The entropy component of the stress $Z_S = T(\partial Z/\partial T)_{LP}$ was then plotted as a function of temperature in order to achieve

some smoothing. The resulting curves were cross-plotted at various fixed values of the temperature to determine the dependence of Z_S on L . Subtraction of each Z_S vs. L curve from the corresponding stress-strain curve then gave the dependence of $Z_H \approx Z_U$ on L .

Figure 6 shows the stress-strain curve obtained for Butyl rubber at $T = T_0 - 40^\circ \text{C}$, with its entropy and enthalpy components. The solid lines are the experimental curves; the corresponding curves predicted by the Guth-James theory are shown by dashed lines. Figure 7 presents the same information for the Paracril rubber, at the reference temperature $T_0 = 60^\circ \text{C}$. In general, Figures 6 and 7 indicate good agreement between the theoretically predicted values of Z , Z_S , and Z_U , and their experimental counterparts. For each rubber,

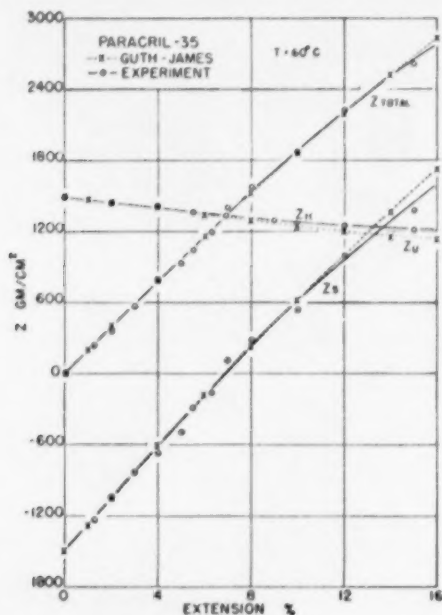


FIG. 7.—Theory vs. experiment for Paracril-35 at 60°C , showing the total stress Z , the enthalpy component $Z_H \approx Z_U$, and the entropy component Z_S as functions of the percentage extension.

however, the theoretical stress-strain curve tends to deviate above the experimental curve at the high extension end. The discrepancies observed in Figure 6 between the theoretical and experimental values of Z_S , and $Z_H \approx Z_U$, are partly the result of experimental error. If the experimental data are internally consistent, then, for the method of fitting described above, the theoretical and experimental values of Z_S and $Z_H \approx Z_U$ must agree at $L = 1$ and $T = T_0$. This conclusion follows immediately from the fact that for both theory and experiment we must have $E_0 = -3Z_S/\alpha T_0 = -3/\alpha(\partial Z/\partial T)_{L,P}$, at $L = 1$ and $T = T_0$. Young's modulus computed from this relation should agree with the value determined from the stress-strain curve at the origin. In this instance, the value of E_0 , computed from the experimentally determined value of Z_S at $L = 1$ and $T = T_0$, is 10.4×10^3 g. per sq. cm. whereas the value obtained

from the experimental stress-strain curve was 9.96×10^3 g. per sq. cm. This error, about 4 per cent, probably results from uncertainties in the determination of the point slopes from the experimental stress-temperature curves.

Comparisons between theory and experiment, similar to those shown in Figures 6 and 7, were also made at several lower temperatures. The same values of K employed earlier were used in these comparisons, since K is assumed to be independent of temperature. Experimental strain values for zero stress were computed with the aid of the linear coefficients of thermal expansion. In each case the theoretical stress-strain curve agreed well with its experimental counterpart, but tended to deviate above the experimental curve at the high extension end. The theoretical entropy and internal energy components showed somewhat stronger deviations from the experimental curves. This was particularly true for the Paracril rubber at low extensions and temperatures.

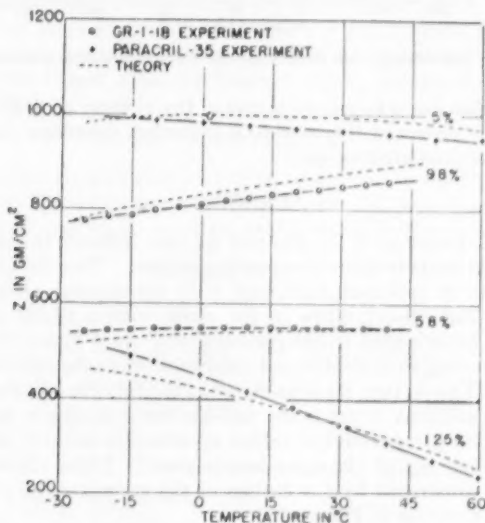


Fig. 8.—Theory vs. observed temperature dependence of stress.

In order to eliminate the influence of uncertainties arising from the evaluation of point slopes, direct comparisons were also made between the theoretical and experimental stress-temperature curves. Figure 8 shows such a comparison for two Butyl curves and two Paracril curves. It appears from Figure 8 that the temperature dependence of the stress predicted by the theory is a little too strong. If the curves were accurately fitted at the high temperature ends, then the theoretically predicted stress values would be too small at the lower temperatures.

Finally, in Figure 9 the observed dependence of the thermoelastic inversion extension on temperature is compared with that predicted by the Guth-James theory for the two rubbers. For the Butyl rubber the theoretically predicted values of the thermoelastic inversion extension appear to be somewhat low. About half of this discrepancy, however, can be ascribed to the previously noted small inconsistency in the Butyl rubber data. The agreement is very good for

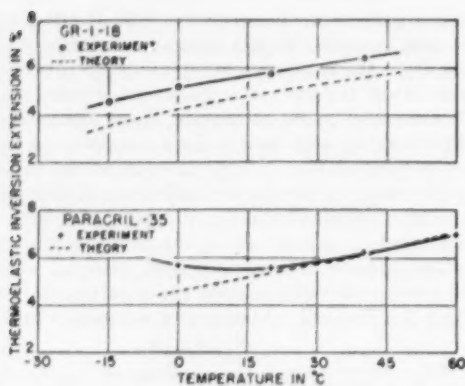


FIG. 9.—Dependence of the thermoelastic inversion extension on temperature.

the Paracril rubber down to temperatures in the vicinity of $+20^{\circ}\text{C}$. At lower temperatures the observed thermoelastic inversion extension deviates sharply upward from the predicted values.

ERRORS

The absolute errors in Z , L , Z_S , and Z_U , are difficult to estimate, and no attempt has been made to show them on the graphs. They involve such factors as nonuniformity in specimen thickness, with consequent variations in cross-sectional areas and uncertainties in the stress values based on these areas. Difficulties are experienced in determining the exact value of the specimen length, corresponding to an unstrained condition, when the specimen is mounted in the clamps. This in turn leads to errors in the relative lengths or percentage extensions. In addition, there is the well-known variation in physical properties encountered in going from one rubber specimen to another, even when both specimens are died out of the same tensile sheet. These errors, taken collectively, are best illustrated by the scatter of the experimental points about the true stress-strain curves of Figure 5.

Percentage extensions are believed to be reliable to better than 0.2 per cent extension, and stress values to better than 0.5 per cent. The values of Z_S and Z_H are probably reliable to no better than 5 per cent, since their determination involves the evaluation of point slopes from the experimental stress-temperature curves.

CONCLUSION

The results of this study may be summarized as follows:

- (1) The agreement observed between theory and experiment is remarkably good in this region of low extensions—almost to within the estimated experimental errors.
- (2) The predicted nonlinear dependence of stress on temperature is confirmed by the experimental data.
- (3) In agreement with the Guth-James theory, the thermoelastic inversion extension is found to be a function of temperature, and is observed to increase with increasing temperature.

(4) Small deviations from the predicted dependence of the stress on temperature are observed. These appear to increase in magnitude with decreasing temperature, and are strongest for the Paracril rubber at low extensions and temperatures. It seems probable that these deviations are the result of intermolecular forces not specifically included in the theory. That the deviations should be stronger for the Paracril-35 rubber is not at all surprising in view of the highly polar nature of the nitrile groups. At the higher temperatures employed in the experiment, such forces may be neglected to a first approximation, because of the greater average distances between molecular groups and the greater thermal kinetic energies. At lower temperatures, however, these forces are no longer negligible, and the molecules exhibit an increasing tendency to "lock-up" as the glassy region is approached.

(5) Finally, an inspection of Figures 6 and 7 reveals a tendency for the theoretical stress-strain curve to lie above the experimental curve at the higher extensions. Recent studies indicate that this is a real deviation, and that it increases rapidly with increasing extension. Similar deviations at somewhat higher extensions have been noted by Treloar⁹ and by Gumbrell, Mullins, and Rivlin¹⁰.

ACKNOWLEDGMENTS

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STRESS RELAXATION IN RUBBER *

I. EVALUATION OF ANTIOXIDANTS

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Study of stress relaxation in rubbers and other elastomers, at constant elongation, has received much attention. The relaxation of stress in an elastomer can occur through viscoelastic flow in the material, or may arise from scission of the hydrocarbon chains supporting the stress. Simultaneously with the rupture of primary bonds, new secondary cross linkages may be formed, causing hardening of the material. A number of authors have discussed the significance of these effects, principally Tobolsky and his coworkers¹.

During stress relaxation at elevated temperature under oxidation conditions, oxygen attack causes chain scission, thus causing degradation; the reversible viscoelastic effect is generally of short duration at these elevated temperatures. Tobolsky, Metz, and Mesrobian² have discussed the relationship between stress relaxation and the number of primary bonds cut, and have determined the number of oxygen molecules absorbed per chain scission. Since degradation of the rubber is caused by chain scission, the stress relaxation should give a fairly direct measure of the degradative effect of the absorbed oxygen. If antioxidant chemicals are incorporated in the elastomer, then the relative rates of stress relaxation will indicate the relative efficiencies of the antioxidants. This will apply whether the antioxidant inhibits the absorption of oxygen or directs the absorbed oxygen into nonactive channels³. This method of evaluation has been suggested by Tobolsky, Prettyman, and Dillon⁴, and has been applied to the comparison of antioxidant chemicals in GR-S stocks by Mesrobian and Tobolsky⁵.

This article described the development of apparatus suitable for the investigation of stress relaxation in rubber, and show how the method can be applied to the evaluation of antioxidant chemicals. A number of stocks have been compared using this technique and the conventional air-oven and oxygen bomb tests, and it is suggested that more rapid and accurate estimates of the antioxidant efficiencies are possible with this than with conventional methods.

APPARATUS

The apparatus has been designed to measure the relaxation of stress in rubber samples held under constant elongation, at elevated temperatures, in air. In the apparatus, provision is made for six samples, each housed in a separate compartment, to be measured simultaneously; the six stress-relaxation curves are recorded on a six-point chart recorder. The stress measurements are made electrically using resistance wire strain gauges. Bonded-type gauges were found to be unsatisfactory for this work and unbonded gauges were designed and constructed for the purpose. The design and construction of a suitable

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gauge have been described⁶. The general layout of the apparatus is indicated in Figure 1.

The six compartments which house the rubber samples are formed by the six vertical tubes, *A* (1 × 12 inch), which run through the tank, *B*. They are heated by circulating a heat exchange liquid from a well-thermostated reservoir. The tank, *B*, is coupled to the reservoir via flexible pipes and is free to slide vertically on the guide rods, *C*. These rods form part of a framework which supports the six strain gauges, *D*, which, in turn, carry thin connecting rods leading to the six steel pulleys which hold the rubber samples, *E*. The lower

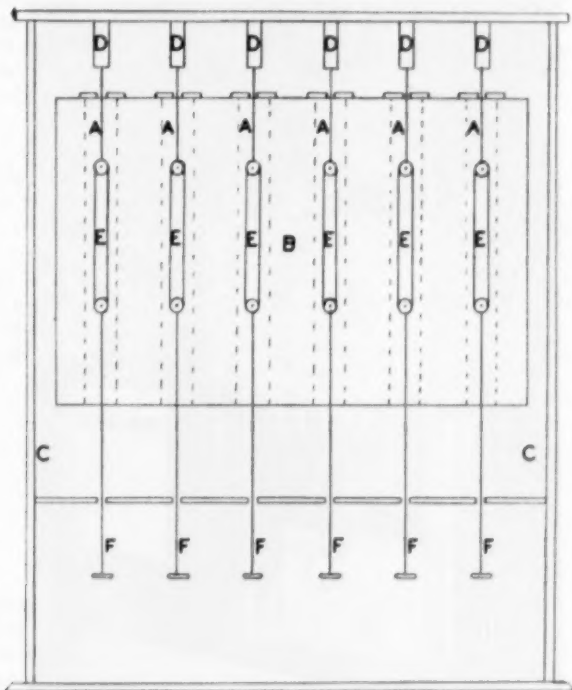


FIG. 1.—General layout of apparatus.

ends of the rubber samples are held by six additional pulleys, mounted on stout rods, *F*, which can be positioned to give any desired extensions. During a test, tank *B* is raised so that the top pulleys are some 2 inches inside the tubes. When this is done, loose fitting disks cover the tops of the tubes. Tests have shown that the temperatures inside the tubes are uniform ($\pm 0.4^\circ \text{C}$) over the regions occupied by samples. Figure 2 is a general view of the apparatus from the front.

The strain gauges, each of which consists of four elements of 15 strands of 46 English standard wire gauge constantan wire, arranged as a Wheatstone bridge network, are designed to withstand a tension of about 1.5 kg. Complete details of construction and design have been published⁶. The gauges are ener-

gized with alternating current at 50 cycles per second. This is derived from a 4-volt winding on a power transformer. The small out-of-balance potential difference across each bridge network is amplified before being fed to a recording potentiometer. The amplifying circuit is shown in Figure 3. The twin-valve balance circuit has been employed to minimize interference from power circuits; this is advisable, since the power frequency is used for operation of the bridge networks. Negative feedback is introduced by the network C_7 , R_{41} , and R_{14} to stabilize the gain. Each gauge is brought into circuit every 30 seconds by a bank of relays operated from a rotating switch synchronized to the six points of

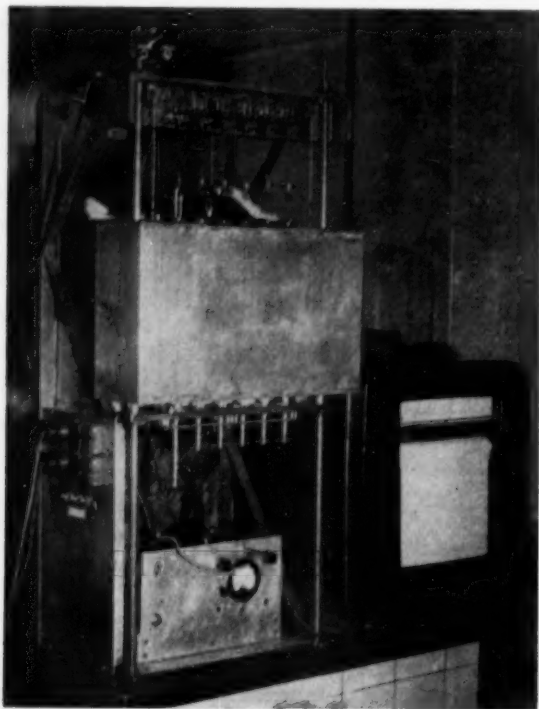


FIG. 2.—Apparatus.

the recording potentiometer. The recorder is an Elliotronic recorder, and since it employs a low impedance magnetic amplifier as a preamplifier, the input to the recorder is connected across a low resistance, R_0 (5 ohms), in series with the 0 to 1 milliamper instrument meter, M , fitted to the output of the main amplifier. Full scale deflection on this meter corresponds to full scale input to the recorder. The bridge networks are balanced, when they are subject to zero load, by means of radio-type potentiometers, R_4 , shown in Figure 3. All the electrical equipment, including the heaters and thermostat controls, is supplied via an electro-mechanical voltage stabilizer, which is stable to within 0.5 per cent.

Preparation of samples.—The apparatus was designed to hold ring-shaped sample specimens about 50 mm. in diameter \times 4 mm. thick and somewhat less

than 1 mm. in radial width. So that direct comparisons could be made with conventional tests, the samples were cut from the same test sheets. These test sheets were 4 mm. thick and, for conventional tests, rings with inner diameter of 44.6 mm. and radial width of 4 mm. were cut with a rotary cutter. By suitably modifying the clamping system, removing the inner blade, and displacing the outer blade 1 mm. outward, it was found possible to cut satisfactory ring samples from the material that remained after removal of the conventional test-specimens. The rubber samples were carefully prepared, and after preliminary experiments had indicated the necessity for standardization of the procedure, the technique of milling a large masterbatch of basic composition, to which the antioxidants and sulfur were added subsequently under well-controlled conditions, was adapted. This procedure led to improved reproducibility of results and enabled comparisons to be made between the various chemicals added to the masterbatch.

EXPERIMENTAL

A study has been made of the effects of various antioxidants on the stress relaxation in natural rubber at elevated temperatures. It is clear from fundamental reasoning that if, as is generally postulated, the relaxation of stress at elevated temperatures is caused primarily by scission of the hydrocarbon chains by oxygen attacks, incorporation of antioxidants will reduce the rate of relaxation. The efficiency of the protective action of the antioxidant should, therefore, be related to the rate of relaxation.

Throughout the work described in this article the following base formulation was used.

	Parts
Pale crepe	100
Precipitated barium sulfate (blanc fixe)	50
Zinc oxide	5
Titanium dioxide	5
Stearic acid	1
Sulfur	2
Tetramethylthiuram disulfide (Thiurad)	0.375
Antioxidant	1

Stocks were cured for 20 minutes at 126° C and molded to sheets 4 mm. thick. Rings of nominal 4- and 1-mm. radial thicknesses were cut from these sheets and, until required, were stored in the dark at a temperature of 0° C. The antioxidants studied were not chosen specifically for this investigation, but they were part of an applicational research program being carried out at the time in the technical service laboratory of Monsanto Chemicals, Ltd. From each masterbatch, about five different stocks were derived; each set of stocks contained a control, usually a stock with no antioxidant, a stock containing an antioxidant of known activity, and two or three containing experimental antioxidants. The 1-mm. sample rings were used for stress relaxation measurements and the 4-mm. samples were subjected to air-oven and oxygen bomb aging. Tensile strength and 300 per cent modulus measurements were made after 0 and 12 days aging in the air oven at 70° C and after 0 and 6 days aging in the bomb at 70° C under 300 pounds per square inch oxygen pressure⁷.

The stress relaxation measurements were made at 100°, 110°, and 120° C. Normally, three samples from each stock were measured at each temperature. The thermostat temperature was adjusted to the appropriate value; time was allowed, in each case, for the temperature to reach equilibrium. With the

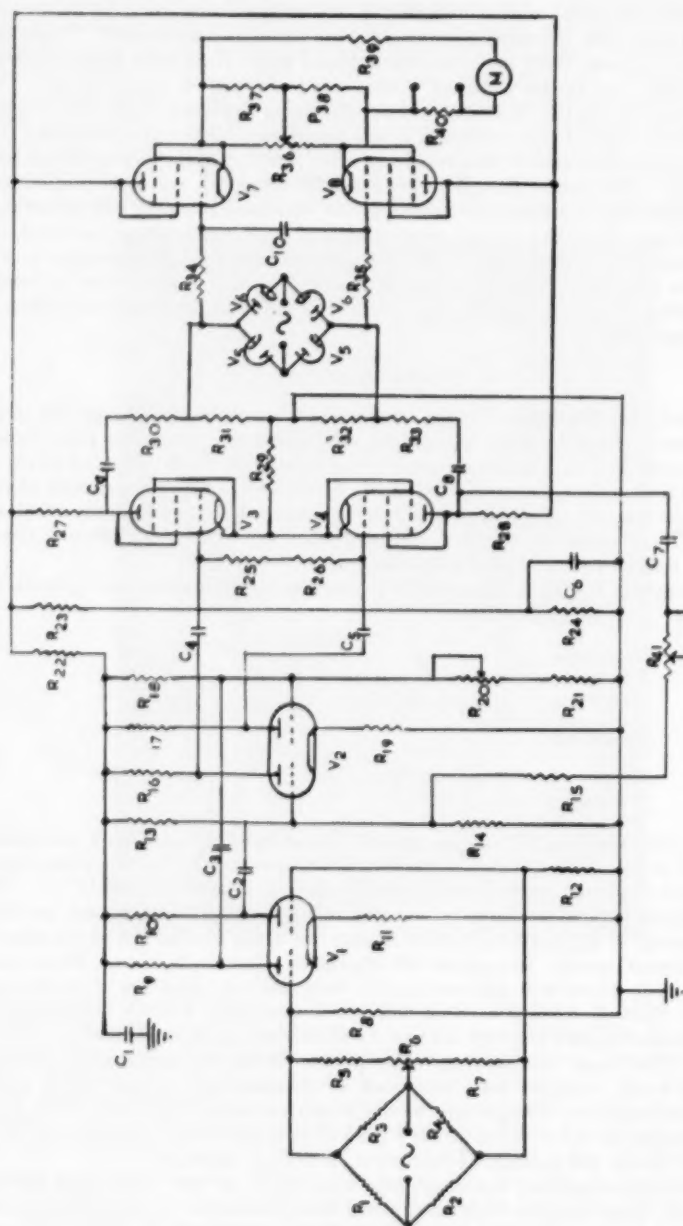


FIG. 3.—Electrical circuit and circuit values.

FIG. 3—Continued

R ₁ , R ₂ , R ₃ , R ₄ = strain gauge elements		Microfarads	
1000 ohms ^a	1000 ohms ^a		
R ₅₄ 10	R ₅₄ 100	C ₁	8
R ₅₅ 1000 (ohms)	R ₅₅ 220	C ₂	0.1
R ₅₆ 10	R ₅₆ 220	C ₃	0.1
R ₅₇ 1	R ₅₇ 15	C ₄	0.1
R ₅₈ 10	R ₅₈ 15	C ₅	0.1
R ₅₉ 10	R ₅₉ 10	C ₆	1
R ₆₀ 220 (ohms)	R ₆₀ 100	C ₇	0.01
R ₆₁ 1	R ₆₁ 100	C ₈	0.1
R ₆₂ 330	R ₆₂ 100	C ₉	0.1
R ₆₃ 100	R ₆₃ 100	C ₁₀	1
R ₆₄ 1 (megohm)	R ₆₄ 100	V ₁	ECC 91
R ₆₅ 20	R ₆₅ 100	V ₂	6 N 7
R ₆₆ 20	R ₆₆ 7.5	V ₃ , V ₄ , V ₅ , V ₆	S P 61
R ₆₇ 330	R ₆₇ 2.2	V ₇ , V ₈	6 H 6
R ₆₈ 4.7	R ₆₈ 2.2	M	0-1 milliammeter
R ₆₉ 50	R ₆₉ 500 (ohms)		
R ₇₀ 68	R ₇₀ 5 (ohms)		
R ₇₁ 4.7	R ₇₁ 1 (megohm)		
R ₇₂ 220			

^a Unless otherwise noted.

tank in its lowest position, the rubber samples were looped lightly over the pulleys. The tank was then raised so that the samples were enclosed in the heated tubes. Meanwhile, the recording potentiometer drive was started, thus initiating the appearance of the six "zero" traces. Any necessary adjustments to the zeros were made during this time. The samples were left in the unstrained positions for 10 minutes to ensure temperature equilibrium; the extension rods were then pulled down, and the catches automatically held them in their new positions. Throughout the investigation the extensions were adjusted to 100 per cent. The stress vs. time curves for the samples were drawn automatically on the 10-inch-roll chart of the recording potentiometer. The absolute values of the stresses could have been found from calibrations of the

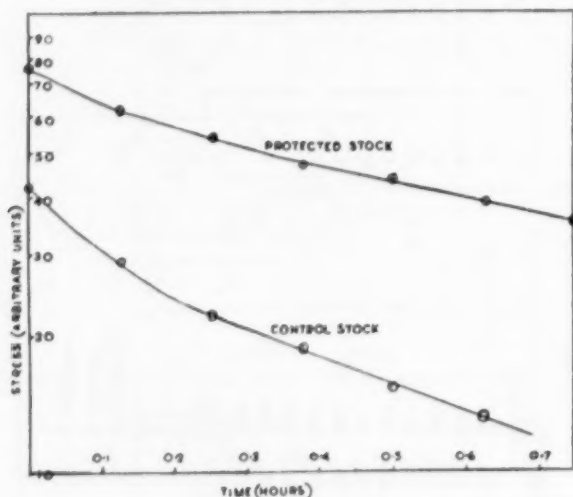


Fig. 4.—Typical stress-relaxation curves.

strain gauges, but for this work such a calibration was unnecessary, since only relative measurements were required. It was verified that the recorder output was directly proportional to the force applied.

RESULTS

Initially, all chart records were transcribed onto logarithmic graph paper, in order to simplify the study of the form of the stress-relaxation curves. Typical examples of such curves are shown in Figure 4. In nearly all cases the log stress vs. time plot showed a rapid initial drop followed by a less rapid linear portion. To a first approximation, therefore, it was assumed that the stress relaxations were exponential and could thus be characterized by a single parameter. The time taken for the stress to relax to half its initial value—the half life—is a convenient parameter to use. The value of this can, of course, be taken directly from the recorder chart, and this procedure was adopted during many of the later measurements.

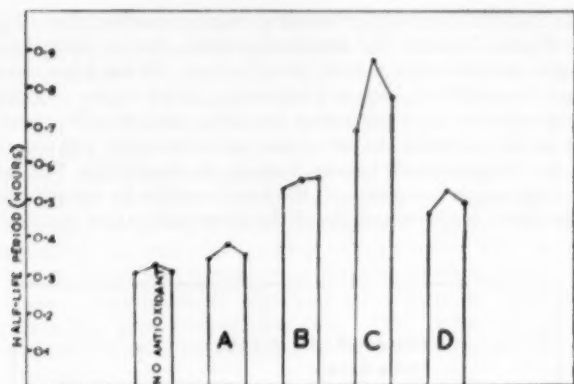


FIG. 5.—Comparison of antioxidants A, B, C, and D, with control stock.

In Figure 5 are shown diagrammatically the half-life periods of a number of different stocks at a temperature of 110°C . These diagrams show how, in one masterbatch, the antioxidant efficiencies can be compared. The reproducibility is good and the discriminating power seems satisfactory. For comparison with the conventional evaluation methods, the stress-relaxation half lives have been plotted as ordinates with either percentage tension strength retained or percentage modulus retained as abscissas. Figure 6 shows stress relaxation results at

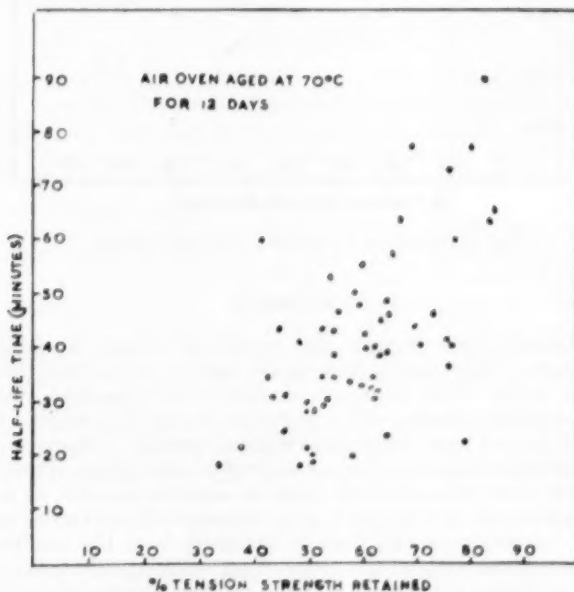


FIG. 6.—Correlation of oven aging with stress relaxation.

110° C plotted against percentage tensile strength retained after 12 days' oven aging, while Figure 7 shows the stress-relaxation results plotted against the tensile strength retained after 6 days' bomb aging. It has been shown mathematically that the points in Figure 6 indicate a (fair) degree of significance in the correlation between stress relaxation and oven aging tensile strength results. For air-oven modulus results the correlation is not so good, but shows a similar trend. For the oxygen-bomb results there is no correlation, but, at least for the series of compounds investigated, the bomb results do not exhibit the even grading range which is characteristic of the stress-relaxation method.

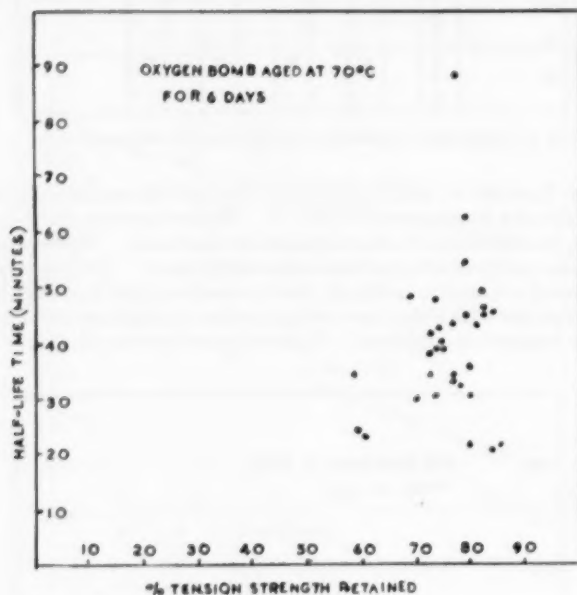


FIG. 7.—Correlation of bomb aging with stress relaxation.

DISCUSSION

Stress-relaxation measurements offer certain advantages in evaluating rubber antioxidants. Chief among these is the rapidity with which the measurements can be made. With apparatus similar to that described, stress-relaxation data on six rubber stocks, with repeats, can be obtained within a day, compared with 12 days or more for the conventional method. Moreover, since the data for one stress-relaxation curve are derived on one sample, rather than as a series of points from measurements made on separate samples, as in the conventional method, the information is more reproducible and can be interpreted more easily. Another striking feature, apparent from the results of stress relaxation on rubbers containing a series of antioxidants, is the discriminating ability. From Figure 5 it is clear that the grading of antioxidants in order of protective efficiency is straightforward.

Although correlation with conventional testing is good, it would be unreasonable to expect perfect correlation, since the measurement of continuous stress relaxation is inherently different from the intermittent measurement of modulus or tensile strength. Fundamentally, if degradative oxygen attack led only to chain scission, which in turn is reflected in the relaxation of stress, then the degree of protection afforded by any antioxidant would be accurately measured by this method. Some complication, however, is introduced in practice when severe cross-linking occurs, since even if it is accepted that slight cross-linking has only a second-order effect on stress relaxation, a high degree of cross-linking introduced during the oxidation process would modify the stress relaxation considerably. Intermittent stress-strain measurements take into account the effects of cross-linking in either case and may, therefore, in the absence of further information, give a misleading idea of the protection afforded by an antioxidant, particularly if the additive catalyzes the formation of cross-linkages in the rubber.

CONCLUSIONS

While it is not possible to say that stress-relaxation measurements can completely replace more conventional methods for evaluation of rubber chemicals and, in particular, antioxidants, it is probable that the method will find increasing and useful application in research and development of such chemicals. For the rapid screening of large numbers of compounds, it will be of great value. Furthermore, in conjunction with conventional modulus and tensile-strength measurements, the stress-relaxation characteristics will provide additional information to enable the relative importances of cross-linking and chain scission to be predicted.

SUMMARY

Conventional evaluation techniques for rubber antioxidants are very time consuming. A method of evaluation based on stress relaxation due to oxidation at elevated temperatures, and an apparatus developed for the study of this phenomenon in a large number of natural rubber stocks, are described in this article. Results are compared with those obtained using conventional air-oven and oxygen bomb aging tests.

The apparatus is suitable for testing six rubber samples simultaneously, and uses unbonded resistance wire strain gauges for the measurement of stresses in the samples. The stress vs. time curves are recorded automatically on a roll chart recording potentiometer. It has been found that the curves approximate to exponential decay curves, and, as such, can be characterized by a single parameter—the half life. This parameter, used as a measure of antioxidant efficiency, can be correlated with the loss of tensile strength for samples aged in a conventional air oven.

The use of the half-life period as a measure of antioxidant efficiency leads to a rapid and easily interpreted method of evaluation for antioxidants in natural rubber. Good reproducibility and discrimination are features of the method.

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II. SIMULTANEOUS OXYGEN ABSORPTION

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The most important effect of oxygen on rubber is the alteration of its mechanical properties which is brought about by a chain scission reaction, the mechanism of which is, at present, not clearly defined. In some cases the mechanism is further complicated by the fact that a cross-linking reaction—i.e., a continued vulcanization—may also take place simultaneously. It has been amply demonstrated by Tobolsky and coworkers¹ that the best way of studying these effects is by stress relaxation measurements of either a continuous or an intermittent nature. Perhaps the most pertinent point in the study of antioxidant protected stocks is the variability, with different antioxidants, of the quantity of oxygen required to bring about a given degradation in properties. It is therefore desirable, in order to obtain an understanding of the mechanism of protection, to study simultaneously a physically measurable quality of the rubber and its oxygen absorption. Throughout the work described in this article, the time taken for the stress in a sample to decay to half its value (the half life) is taken as a measure of the protective action of the incorporated antioxidant.

A technique developed for the study of intermittent stress relaxation has been described previously². In this method the sample was in the form of a circular disk of rubber, which was intermittently distorted by subjecting it to oxygen pressure. Later developments of this method enabled the modulus of the rubber, viz., the G parameter of the kinetic theory of elasticity, to be deduced from the volume-pressure readings during distortion of the rubber. Unfortunately, the permanent set which developed after a few cycles of this procedure rendered invalid the equations used to deduce the value of G . The difficulty of allowing for this effect considerably decreased the value of the method, and an apparatus was therefore developed in which the sample was distorted by a simple one-dimensional extension. The details of a new method of measuring stress relaxation and simultaneous oxygen absorption and the use of the method for a study of antioxidant protection are described in this article.

APPARATUS

The apparatus is shown diagrammatically in Figure 1. Essentially, it consists of two portions concerned with the measurement of stress and oxygen

absorption, respectively. The stress measurement section comprises the bellows, B_1 , contact, C_1 , manometer, M_1 , and electrolytic cell, E_1 . The rubber sample, R , in the form of a band, 170 mm. in circumference, 4 mm. wide, and 1 mm. thick, is suspended between two hooks within a mild steel jacket around

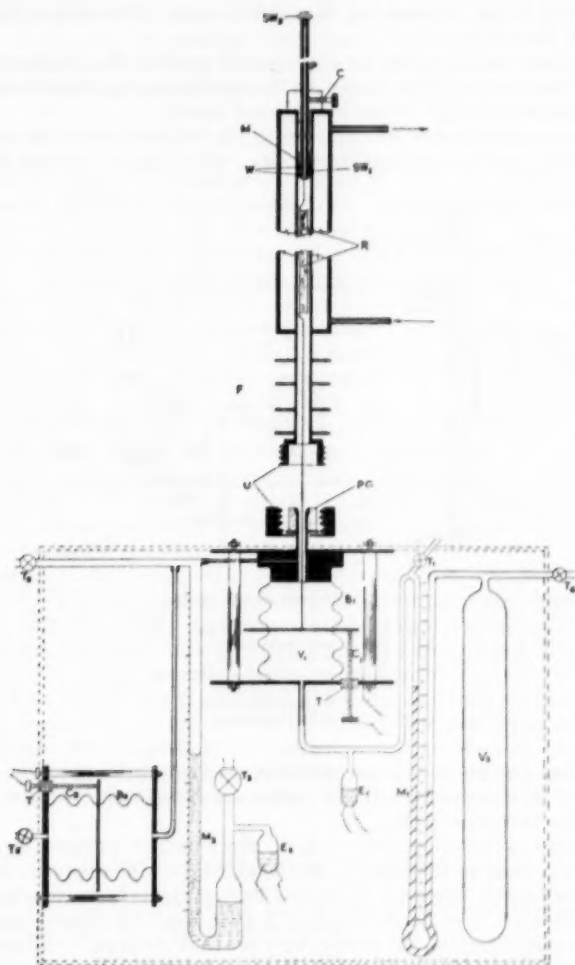


FIG. 1.—Stress relaxation-oxygen absorption apparatus.

which hot liquid is circulated from an accurately controlled thermostated bath. During the experiment the position of the upper hook is rigidly fixed by clamping tube P at C . The lower hook is attached to the central plate of the bellows, B_1 , the top and bottom of which are rigidly fixed, and the plate will, therefore, respond to changes of stress in the rubber. When the sample is extended, the

central plate is raised and the contact, C_1 , is broken. This contact is insulated from the metal part of the bellows by the Tufnol plug, T . The contact may now be remade by adjusting the pressure in V_1 , the portion of B_1 remote from the rubber—this is done through T_1 . The pressure difference required to balance the stress may be read directly in centimeters of mercury from the scale attached to the manometer, M_1 ; this pressure difference is directly proportional to the stress.

To eliminate variation due to atmospheric pressure fluctuations, the open side of the manometer is connected to the enclosure, V_2 , which is sufficiently large to maintain linearity of reading against stress.

During the experiments, as the stress in the rubber decays, the contact, C_1 , is made. This activates a thyatron relay, which passes current in the cell,

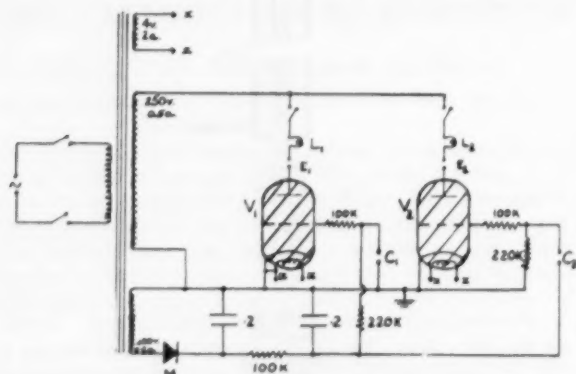


FIG. 2.—Electrical control circuit.

- V_1, V_2 = Gas-filled triodes
- L_1 = 60-watt lamp
- L_2 = 40-watt lamp
- E_1, E_2 = Electrolytic cells
- C_1 = Stress contact
- M = Metal rectifier

E_1 , and the gas so generated increases the pressure in V_1 until the contact is rebroken. A continuous record of the stress in the sample is thus obtained by observing the manometer, M_1 .

The oxygen absorption system is of the constant pressure type, and is essentially the same as that used in previous work². The only modification is the introduction of a new type of control device, the bellows arrangement, B_2 , which operates on a principle similar to that used for stress measurement. When oxygen is absorbed, the momentary pressure drop pulls the central plate of B_2 to the right and breaks the contact, C_2 . This activates a thyatron relay, which passes current in the cell, E_2 , which forces liquid up the tube, M_2 , until the original pressure is restored and the contact, C_2 , is remade. The pressure is, therefore, kept at a constant value and the liquid rise in M_2 is a direct measure of the oxygen absorbed and may be observed on the attached scale.

The portion of the apparatus enclosed within the dotted lines of Figure 1 is contained within a thermostated box accurately controlled at a temperature of 34° C, and in order to minimize the heat conducted from the hotter parts of the

apparatus to the box, cooling fins F are fitted to give a steep temperature gradient down the tube. The tube, P , is provided with a sliding gastight fit by the silicone rubber washer, SW_1 , which is supported by, and compressed between, two mild steel washers, W . This is, in effect, a silicone rubber piston ring, which is covered with mercury at M to complete the seal.

The electrical circuit is shown in Figure 2. Parts V_1 and V_2 are gas-filled triodes; V_1 is arranged to conduct when contact C_1 is close and V_2 conducts when C_2 is opened. The lamps, L_1 and L_2 , control the currents in the electrolytic cells and also act as indicators.

PROCEDURE

To place the sample in position the union, U , is broken (this is made gastight by means of the polythene gasket, PG) and the heating jacket is raised until the lower hook is exposed; P is lowered to expose the upper hook. The sample is placed over the upper hook, and P is raised so that it engages on the lower hook; the jacket is lowered and fixed in position, while P is held at a fixed height to keep the sample in an unextended state. The apparatus is flushed with oxygen, which is admitted through T_2 and passed out through T_3 via M_2 and through SW_2 via P . Tube P is raised to give the required extension, and the oxygen flow is cut off and the apparatus is sealed. The pressure in V_1 is adjusted until C_1 is making and breaking, and T_1 and T_2 are closed. The relays are switched on and the system rapidly reaches equilibrium. When both relays are operating, the operator begins to read M_1 and M_2 . This is usually 5 minutes after the sample is extended. Taps T_4 and T_5 are kept closed at all times to eliminate any effects due to changes in atmospheric pressure. In the present system, C_2 is adjusted so that oxygen is absorbed at a pressure of 765 mm. of mercury.

Preparation of specimens.—The test bands were cut from standard sheets, 4 mm. thick³. The normal procedure was first to cut from the sheet a standard ring 4 mm. in radial width, as for normal technological evaluation of rubber stocks, using a two-blade rotary cutter with radii of 26.3 and 22.3 mm. An auxiliary foot, 26.5 mm. in radius, was then attached to the foot of the cutter, and the test band just less than 1 mm. thick was cut with a single cutter appropriately positioned. This method of cutting was developed primarily for the preparation of test-specimens for an investigation of rubber antioxidants, using the normal technological test methods on the 4-mm. ring and the stress-relaxation methods on the 1-mm. ring. Sampling errors were thus largely eliminated.

REPRODUCIBILITY OF EXPERIMENTS

The accuracy of the apparatus and sample production was investigated. For this purpose the following stock was used:

	Parts
Pale crepe	100
Zinc oxide	3
Stearic acid	0.5
Sulfur	3
Diphenylguanidine	0.5

The stock was cured for 60 minutes at 142° C (the conditions for optimum cure). In Table I the results for two different mixes and for different sheets within

mixes are presented. The results show clearly that, within a given mix, the reproducibility is satisfactory, but the variation between mixes is too great to allow valid comparisons to be made between stocks that are separately mixed. An improved method of masterbatch mixing was introduced to overcome this difficulty. This method consisted of milling a large amount of rubber and adding all ingredients except sulfur and the antioxidants to be compared. The mix was then split into parts, and the appropriate antioxidant and sulfur was added to each part in a short well-controlled mix. The separate stocks were subsequently vulcanized into 4-mm. sheets under identical conditions. The method was tested by comparing three nominally identical masterbatches; each

TABLE I
REPRODUCIBILITY OF EXPERIMENTAL DATA

Sample no.	Half life (min.)	Three-quarter life (min.)	Oxygen absorption, (cc./gram)	
			Half life	Three-quarter life
Mix 1, Sheet 1				
1	11	22	1.5	2.7
2	11	21	1.5	2.6
3	10	20	1.6	2.8
4	11	22	1.7	3.0
Mix 1, Sheet 2				
1	10	20	1.8	3.0
2	10	20	1.6	2.6
3	11	21	1.4	3.2
4	11	22	1.5	2.5
Mix 2, Sheet 1				
1	16	30	1.4	2.4
2	18	36	1.7	3.0
3	16	32	2.0	3.7
4	16	32	1.5	2.8
Mix 2, Sheet 2				
1	16	32	1.4	2.5
2	15	20	1.3	2.4
3	15	31	1.5	2.8
4	16	32	1.4	2.5

batch was divided into six stocks, each containing a different antioxidant. The results showed clearly that, whereas comparisons between antioxidants within each masterbatch were the same, the absolute values in the three cases varied considerably. It was, therefore, possible to proceed to a comparison of antioxidants with some degree of confidence.

CORRELATIONS

Two methods of correlating oxygen absorption and protection, as measured by half life, are used. One method is the evaluation of the number of molecules of oxygen absorbed per chain cut; and second, correlation is based on an index expressed simply by the ratio of the aging properties to the absorption properties.

The number of molecules of oxygen absorbed per chain cut is evaluated as follows. It can readily be shown⁴ that, by making certain assumptions, if q is the number of cuts per gram of rubber, N_0 the number of chains supporting the initial stress, ρ the density of the rubber, and f_0 and f the stress initially and at time t , respectively:

$$q = -\frac{N_0}{\rho} \ln \frac{f}{f_0} \quad (1)$$

and using the equation derived from the kinetic theory of elasticity⁵ with the usual notation:

$$f_0 = N_0 K T \left(\alpha - \frac{1}{\alpha^2} \right) \quad (2)$$

where α is the extension ratio, thus:

$$q = -\frac{f_0}{K T \left(\alpha - \frac{1}{\alpha^2} \right) \rho} \ln \frac{f}{f_0} \quad (3)$$

that is, q is proportional to the natural logarithm of the fractional stress decay; the constant of proportionality may readily be evaluated in any particular case. Thus a plot of $\log f/f_0$ vs. oxygen absorbed results in a curve whose slope may be used to calculate the number of cuts per molecules of oxygen.

The evaluation of the aging index, V , suggested by Le Foll⁶, results in a measure of the protective action of the antioxidant compared with the control in the same masterbatch. This is simply the ratio of the half life of the control to that of the antioxidant stock; it is unity if no additional protection is afforded. Similarly, O , the oxidizability index, is the ratio of the rates of absorption of the antioxidant stock and the control stock. The coefficient of deactivation, D , is simply the ratio, O/V . This coefficient is greater than unity for a deactivating effect, e.g., if the protective action is better than that afforded simply by the reduction in the rate of absorption, the oxidizability index is greater than the aging index and D is greater than unity.

EXPERIMENTAL RESULTS

The actual data obtained in an experiment yields three curves—oxygen absorption against time, stress decay against time, and stress decay against oxygen absorbed. A typical example of the curves from this experiment is shown in Figure 3. The investigations were all carried out at a temperature of 120° C; the sample was held at 100 per cent extension. In each case duplicate experiments were performed, and in most cases the reproducibility was good, especially for the half life and the rate of oxygen absorption determination. All oxygen absorption rates are given in cc. per (gram) (hour), measured at 34° and 765 mm. of mercury.

The stocks of Table II were compounded using the same formulation used by Le Bras⁷, adopting the masterbatch technique, in order to investigate his deactivation theory. Although the cure time used by Le Bras was 8 minutes at 143° C, a range of cures was investigated.

The results obtained in this series are presented in Table III; each value is the mean of duplicate measurements. III shows that mercaptobenzimidazole has in one case (stock C with the higher concentration) an activating effect. The low half life of mercaptobenzimidazole indicates that the protective action

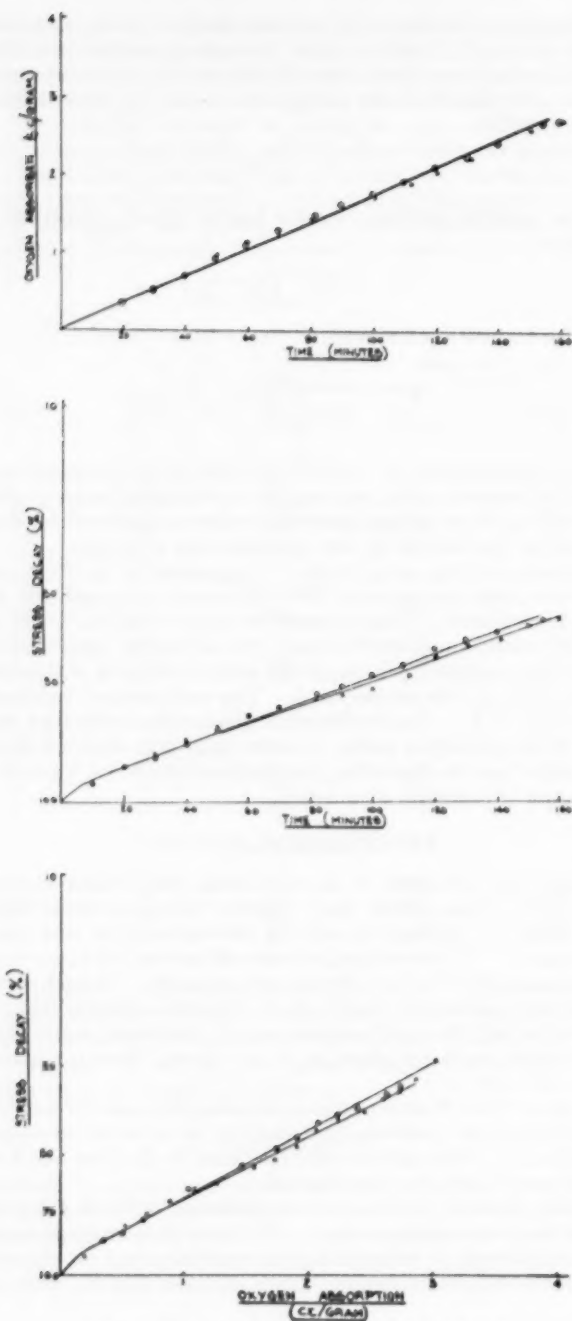


FIG. 3.—Stress relaxation and oxygen absorption at 120° C.
Stock 4 of Table IV.

TABLE II
LE BRAS FORMULATION OF STOCKS

	Le Bras formulation (Parts for stock)					
	A	B	C	D	E	F
Pale crepe	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5
Devolite clay	10	10	10	10	10	10
Benzothiazolyl disulfide (Thiofide)	0.25	0.25	0.25	0.25	0.25	0.25
Tetramethylthiuram disulfide (Thiurad)	0.2	0.2	0.2	0.2	0.2	0.2
Phenyl-2-naphthylamine	—	1.5	—	0.75	0.75	—
Mercaptobenzimidazole	—	—	1.5	0.75	—	0.75
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5

is poor. This apparently contradicts the findings of Le Bras, but agrees with the work of Shelton and Cox⁷, who suggested that the effect of mercaptobenzimidazole on the state of cure may be a contributory factor to its action. It is obviously, in part at least, a "normal" antioxidant, since in all cases investigated, it produces an oxidizability index that is less than unity.

It is clear that mercaptobenzimidazole has a slight activating effect, measured by coefficient *D*, except when the stock with 0.75 part of mercaptobenzimidazole was cured for 10 and 12 minutes; a deactivating effect was shown in

TABLE III
INVESTIGATION OF LE BRAS DEACTIVATION THEORY

Stock (Table II)	Half life (min.)	Oxygen absorption rate (cc./g./hr.)	Molecules oxygen/ chain cut	Aging index (V)	Oxidizability index (D)	Coefficient of deactivation (D)
Cured 8 minutes						
A (control)	32	2.45	0.92	—	—	—
B	62	1.33	1.03	0.52	0.54	1.04
C	36	1.47	0.72	0.89	0.60	0.68
D	82	1.15	1.22	0.39	0.47	1.21
E	—	—	—	—	—	—
F	39	1.59	0.80	0.82	0.65	0.79
Cured 10 minutes						
A	29	2.37	0.77	—	—	—
B	66	1.42	0.88	0.44	0.60	1.37
C	34	1.52	0.59	0.85	0.65	0.76
E	51	1.54	0.85	0.57	0.65	1.14
F	41	1.90	0.96	0.71	0.80	1.12
Cured 12 minutes						
A	33	2.42	0.73	—	—	—
B	80	1.09	0.71	0.41	0.45	1.10
C	38	1.44	0.59	0.87	0.60	0.69
D	88	1.23	1.19	0.38	0.51	1.15
E	55	1.67	0.90	0.60	0.69	1.05
F	54	1.55	0.81	0.61	0.64	1.33

these cases. The effect of cure time in all cases (except at 0.75 part of mercaptobenzimidazole) is slight. The variation introduced by altering the concentration of antioxidant is interesting. In the case of phenyl-2-naphthylamine the behavior is normal; the lower concentration giving rise to more rapid deterioration and absorption. The action of mercaptobenzimidazole is anomalous in that, while the absorption rate increases with decreasing concentration, the protective action also increases. On the whole, the molecules absorbed per cut parameter tend to decrease with increasing cure time.

The data obtained are a good indication of the reproducibility of the method and of the compounding of stocks. Therefore, a number of accepted antioxidants were investigated to see if significant differences existed in the resulting molecules per cut parameter or the deactivation coefficient and, hence, in their mode of protection. Although the Le Bras theory was confirmed in the case of mercaptobenzimidazole, the blend of phenyl-2-naphthylamine and mercapto-

TABLE IV
EFFECT OF ANTIOXIDANT BLENDS

Stock No.	Antioxidant	Half life (min.)	Oxygen absorption rate (cc./g./hr.)	Molecules oxygen/chain cut	Aging index (V)	Oxidizability index (O)	Coefficient of deactivation (D)
1	None (control)	21	2.69	0.80	—	—	—
		20	2.38	0.83	—	—	—
2	Phenyl-2-naphthylamine	61	1.25	0.86	0.34	0.49	1.45
		55	1.33	0.74	0.37	0.52	1.41
3	Acetone-aniline condensation product	88	1.23	0.93	0.23	0.49	2.13
		84	1.21	0.88	0.24	0.48	2.00
4	Acetone-diphenylamine condensation product	94	0.99	0.80	0.22	0.36	1.79
		98	0.99	0.94	0.21	0.39	1.85
5	Alkylated phenol sulfide	56	1.36	0.85	0.37	0.54	1.45
		62	1.26	0.82	0.33	0.50	1.52
6	<i>N</i> -cyclohexyl- <i>N'</i> -phenyl- <i>p</i> -phenylene-diamine	180	0.94	1.27	0.11	0.37	3.33
		175	0.80	1.17	0.12	0.32	2.63
7	Alkylated phenol	38	1.45	0.78	0.54	0.57	1.05
		38	1.50	0.86	0.54	0.59	1.09
8	Mercaptobenzimidazole	38	1.36	1.07	0.54	0.54	1.00
		35	1.50	1.02	0.59	0.59	1.00
9	Phenyl-2-naphthylamine-mercaptobenzimidazole	50	1.06	0.97	0.41	0.42	1.02
		57	1.09	0.95	0.36	0.43	1.19
10	No. 3-Mercaptobenzimidazole	75	0.95	0.84	0.27	0.37	1.37
		73	0.95	0.87	0.28	0.37	1.32
11	No. 5-Mercaptobenzimidazole	48	1.11	0.74	0.43	0.44	1.02
		55	1.11	0.82	0.37	0.44	1.19

benzimidazole produced a synergistic protective effect, in that the combination resulted in better aging properties than were produced by either alone. This effect was found to be much more pronounced in diphenylguanidine accelerated stocks. Blends of other antioxidants with mercaptobenzimidazole were investigated to ascertain whether this effect was general. The results of this program are given in Table IV. The Le Bras formulation was used with 1.5 parts of antioxidant and 0.75:0.75 blends; the samples were cured for 10 minutes at 143° C.

The results were all obtained at 120° C. Mercaptobenzimidazole (Stock 8) exerts no apparent deactivating effect—a confirmation of the previous work. All other antioxidants examined exhibit this effect to a greater or lesser degree. The blends are in all cases slightly less protected, measured by half life, than the corresponding antioxidant stock, but it must be remembered that this degree of protection is maintained with only half the quantity of the primary antioxidant. It is probably assisted by the increased protection afforded by half the concentration of mercaptobenzimidazole as observed previously.

In order to obtain a more complete picture of the effect of cure on the Tobolsky equation⁴ by altering the value of N_0 , a control stock (formulation A, Table II) was mixed and cured for various times to give a range of modulus values. The results are given in Table V. In this case it is not possible to evaluate V , O , and D , since no stock may be regarded as a standard control.

INTERPRETATION OF STRESS RELAXATION DATA

In an attempt to interpret the stress-relaxation data in terms of the molecular network the method of Tobolsky and coworkers⁴ has been used. According to the equations derived, the number of molecules of oxygen required to cut a molecular chain between cross-links may be determined. It is believed, however, that the assumptions implicit in the derivation are open to certain criticisms which render the method invalid. The criticisms fall into two classes—the neglect of chain ends and network defects and the effect of the cutting of one chain on surrounding junction points is not considered.

It is assumed that initially all units of the rubber molecule are between cross links and contribute to the support of stress. It has been shown⁸ that network defects, such as loose chain ends and intramolecular cross-links, do, in fact, occur and give rise to a certain fraction of ineffective chains. In order to correct the derivation of the formula for the number of cuts produced by this effect, the initial fraction of ineffective polymer must be known. The methods used for this type of study⁹ have been approximate, owing to the complexity of the problem, but the work of Gee¹⁰ on the comparison of the degree of cross-linking, estimated by physical and chemical methods, indicates that the fraction of ineffective polymer is not small.

It is also implicitly assumed that, when a chain is cut, the break has no effect on surrounding chains and junction points (cross-links). In an attempt to correct for this, the elastic energy stored in the rubber was considered to be divided equally among the effective chains—corresponding to the free energy. If at any time the energy stored in each chain is e , the energy liberated in a single cut will be $e(1 + \alpha)$, where α is a parameter which depends on the relaxation of neighboring chains. This energy is dissipated by internal viscous damping as the surrounding chains take up new equilibrium positions. The simplest possible assumption is that α is a constant, which will be the case when the degree of degradation is small, and in this case the number of cuts in term of α and the energy in the rubber at any time can be evaluated. The energy stored in the rubber cannot be found from stress-relaxation data, because the permanent set is due to a combination of the effect described above with additional cross-linking reactions, which are known to take place in the presence of oxygen. This theory is supported by the fact that when the tension has decayed almost completely, the sample still possesses good elastic properties. This cross-linking further complicates the molecular interpretation of stress-relaxation data, and differences observed between antioxidants may, in part at least, be due to their different effects on this process. In view of these arguments, the derived value of the number of molecules of oxygen absorbed per chain cut is very unreliable for use in the correlation of oxygen absorption and stress-relaxation data.

The results of Table V show clearly the variation in this parameter for different degrees of cure of the same stock. When the initial modulus (proportional to N_0) is small, the number of molecules of oxygen per cut is large. If it is assumed that each cut corresponds to one reacted isoprene unit, it would be

TABLE V
EFFECT OF CURE TIME
Formulation A of Table II

Cure time (min.)	Half life (min.)	Oxygen absorption rate (cc./g./hr.)	Molecules oxygen/chain cut	No. of chains/unit vol./ ($N_0 \times 10^{-3}$)
20	37	2.15	1.95	0.491
22.5	40	2.20	1.33	0.679
25	30	2.54	1.19	0.799
27.5	29	2.51	0.92	0.884
30	31	2.52	0.82	0.935
35	39	2.29	0.78	0.967

expected that the values in all cases should be equal, since cuts on chains previously cut have been allowed for in the derivation on the formulas. The discrepancy is probably due to the assumptions implicit in the derivations, since a looser network (the more lightly vulcanized stocks) will probably differ in the percentage of polymer not included between cross-links. It is also possible that the effect on surrounding junction points when one chain is cut will differ with the degree of cure.

If it is assumed that the discrepancy is due entirely to the variation in the fraction of polymer present as effective chains, the derivation of the formulas may be amended to include this assumption. If the fraction of polymer present as effective chains is β , the equation for the number of cuts produced per unit volume when the stress has decayed to f is:

$$q = -\frac{N_0}{\rho\beta} \ln \frac{f}{f_0} \quad (4)$$

The values obtained for the number of molecules of oxygen absorbed must be multiplied by β to correct for network defects. If it is assumed that the stock with the highest cure consists almost entirely of effective chains, the values of β for other cure times may be found, as follows:

Cure time (min. at 125° C)	β	Av. mol. wt. between cross-links
20	0.39	4800
22.5	0.58	5100
25	0.65	4900
27.5	0.84	5700
30	0.94	6000
35	1.00	6200

The average molecular weight is calculated by assuming that molecular weight $= \beta\rho/N_0$. The increasing molecular weight between cross-links is obviously in error, and is probably in part due to neglect of the effect of cuts on surrounding junction points.

The idea of the chain-cutting processes relaxing neighboring chains introduces a consideration of the randomness of the process. A systematic cutting procedure could bring about a much greater stress relaxation than an equivalent degree of random cutting and, hence, nonhomogeneously dispersed antioxidants or other compounding ingredients could give rise to variation of stress relaxation for a given absorption. This point arises in considerations of the dispersion of

certain accelerators in rubber when poor dispersion is known to give rise to localized overcuring. Similarly, a poorly dispersed antioxidant could give rise to localized protection and, hence, a nonrandom chain scission.

The difficulties of molecular interpretation are so great that it is more convenient, though less general, to grade antioxidant action by what is known as the deactivating effect. Le Bras¹¹ suggested two types of mechanism for antioxidant action, the normal case in which the antioxidant simply inhibits the absorption of oxygen and retards aging in the same proportion and, secondly, a type of antioxidant termed a deactivator, which decreases the rate of degradation to a much greater degree than they affect the oxygen absorption. Le Foll⁶ proposed the use of the coefficient of deactivation, D , which, in the notation of the present article, is proportional to the product of the half life and the absorption rate. This coefficient expresses quantitatively the amount of oxygen required to reach a given stress decay. The variation of the values of D obtained with the antioxidants studied demonstrate clearly the fact that any description of oxidative degradation in terms of either oxygen absorption or decay of physical properties alone is essentially incomplete. The coefficient, D , correlates the oxygen absorption with stress relaxation and is used as an indication of the mechanism of protection.

The comparison between the results of this work and those reported by Le Bras¹² and Shelton⁷ is perhaps unfair, since Le Bras and Shelton used technological methods of evaluating aging resistance, and the same aspect of antioxidant action was not studied. The technological test is also subject to a high degree of error, especially when the property being measured is tensile strength, and on these grounds it is not very useful in fundamental studies. It should also be remembered that the technological tests are intermittent, i.e., the sample is aged in the relaxed state and then tested, and they would probably compare more favorably with intermittent modulus measurements. The present apparatus is not capable of this, but an apparatus has been designed on the same principles for this work. The advantages of the present apparatus over the technological testing are that the method is shorter and nondestructive, and direct correlation with absorption is obtained.

The role of mercaptobenzimidazole as a deactivator cannot be supported by the evidence reported with respect to stress relaxation. Its behavior at half concentration is, however, anomalous and merits further study. Further study might explain the discrepancy between the authors' results and those of Le Bras. The effect appears to be more pronounced with longer cure times.

The sample thickness of approximately 0.9 mm. is free of diffusion effects at 120° C. This is evident from the literature¹³ and also from preliminary work. In all cases the absorption indicates the level of oxidation to be at the constant rate stage, since the curves in all cases are linear except for a short initial portion where nonlinearity is due to temperature variation in the apparatus. The relaxation curves, the logarithm of the stress decay plotted against time, are linear after a short initial portion. In cases where the oxygen-log stress curves were not linear, the slope at the half life was used to calculate the number of molecules of oxygen per cut.

While it is not possible to make any fundamental deductions from the results of this work, they do indicate that, for a complete description of the mechanism of degradation, both oxygen absorption and physical degradation should be considered. The method of evaluation is suitable.

SUMMARY

In any serious study of antioxidant action, it is essential that the oxygen absorption rate of a protected rubber be determined and the changes in the network system caused by the oxygen be assessed. This information is normally obtained from separate oxygen absorption and aging studies. A method is described in this article which enables simultaneous measurements of oxygen absorption and stress relaxation to be made on a given rubber sample.

A number of antioxidants have been compounded with natural rubber and, from the results, an estimate is made of the molecules of oxygen absorbed per rubber chain cut. This is found to vary with the antioxidant, although some difficulties of interpretation are pointed out. Variations of deactivating effect among the antioxidants shows clearly that any attempt to understand oxidative degradation in terms of oxygen absorption or decay in physical properties alone is not possible.

The method provides a new technique that is of value in any basic study of antioxidant action in elastomers.

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STRESS RELAXATION OF VULCANIZED RUBBER IN COMPRESSION AND TENSION *

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Stress relaxation is an important consideration in determining the suitability of gasket materials for Navy door hatches, pipe lines, and similar applications. In view of this, the Material Laboratory, New York Naval Shipyard, has devoted considerable time and effort to the design of equipment to measure stress relaxation of rubber materials deformed in compression and in tension.

COMPRESSIVE STRESS RELAXATION APPARATUS

A cross-section of the Material Laboratory compression stress relaxation apparatus, drawn to scale except for the 3-inch dimension shown for the height of the bushing support, is shown in Figure 1. This apparatus is essentially the same as that used to measure the compression set of vulcanized rubber at constant deformation¹. The test-specimen, which is a cylinder 0.5 inch thick by 1.129 inches in diameter, is compressed to the desired deformation between two parallel steel plates. These plates are bolted together to the height of the inserted metal shims, which limit the percentage deformation of the specimen. The part of the top-plate assembly that actually compresses the specimen is a load applicator. The load applicator can slide with minimum friction with respect to the top plate, and is insulated electrically from the apparatus except for a flange that is in metal-to-metal contact with the underside of the top plate. An electrical resistance meter connected to the apparatus measures the resistance at the metal-to-metal contact of these parts.

The arrangement of the apparatus is such that the back stress in the compressed specimen exerts on the load applicator an upward force that is resisted by the top plate. An external force applied to the load applicator decreases the force of the top plate on the load applicator (the sum of these two forces is equal to that exerted by the compressed specimen). The external force, which is increased gradually, causes additional compression of the specimen only when it exceeds the back force in the specimen. When this condition occurs, the additional compression of the specimen results in physical separation of the load applicator from the top plate, which is detected on the meter as a change in the contact resistance between these parts. The instant this separation occurs, the force of the top plate on the load applicator is zero, and the back force exerted by the specimen is equal to the external force supplied by the load-measuring device. Since the weight of the load applicator itself exerts a force to compress the specimen, its weight is added to the external force reading. The bottom plate of the apparatus has a base plug with a micrometer arrangement, so that each division on the underside of the plug corresponds to a relative elevation of 0.001 inch of the plug with respect to the bottom plate. This plug makes possible accurate adjustment of the percentage of compression of the specimen.

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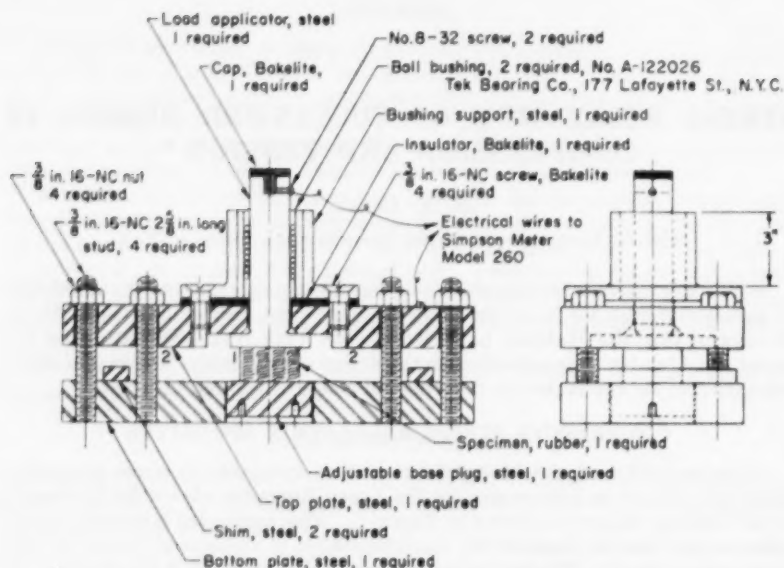


FIG. 1.—Cross-section of the Material Laboratory compression stress relaxation apparatus.

PROCEDURE

In making a test, the height of the specimen is measured. Then the apparatus is adjusted to compress the specimen to the desired deformation. At 3 min. (± 10 sec.) after the specimen is compressed, the back force exerted by the unaged specimen is determined. The external force is then removed, and the assembled apparatus is allowed to condition for 1 hour at room temperature. At the end of the 1-hour period, the apparatus is subjected to the desired aging conditions. After aging, the back force exerted by the specimen is again determined. Once the stress relaxation apparatus is assembled, no additional manipulation of the specimen is required, regardless of the number of times the back force is measured. This is because only about 0.0005 inch additional compression of the specimen is required to measure the back force. When the aging is done at elevated temperatures, the specimen is allowed to cool at room temperature for 5 hours ($\pm \frac{1}{2}$ hour) to attain thermal equilibrium.

TENSILE STRESS RELAXATION APPARATUS

The tensile stress relaxation apparatus is shown in Figure 2. This apparatus consists essentially of a removable test jig to maintain a T-50 type specimen at a desired elongation, and with provision for measuring the back force in the elongated specimen. The T-50 specimen is elongated between the stationary clamp and a clamp secured to an aluminum rod fitted with a pin that fits into a V-slot in an adjustable collar positioned on the jig. This collar resists the restoring force of the elongated specimen. After assembly, the test jig is positioned on the apparatus so that the top of the aluminum rod can be secured to a flexible linkage, which in turn is connected to a 500-gram capacity Hunter

spring gauge. The Hunter gauge is secured to a bracket that can be elevated or lowered relative to the test jig by turning a thumb screw (not shown in Figure 2).

The arrangement of the apparatus is such that, when the Hunter gauge is elevated, the load on the gauge is transferred to the specimen. When this load is less than the back force in the specimen, the rate of load increase on the gauge is directly proportional to the movement of the thumb screw, due to the linear relationship between load and elongation of the spring in the gauge. However, when this load is greater than the back force in the specimen, the specimen elongates further. Additional elongation of the specimen is detected visually as a break or discontinuity in the rate of load application with movement of the thumb screw. This test is very sensitive, and only a slight additional elongation of the specimen is required to obtain a reading of back force. Having measured the back force, the external load due to the Hunter gauge is removed. The restoring force of the specimen is then automatically reapplied on the collar. The assembled test jig is then removed from the apparatus and

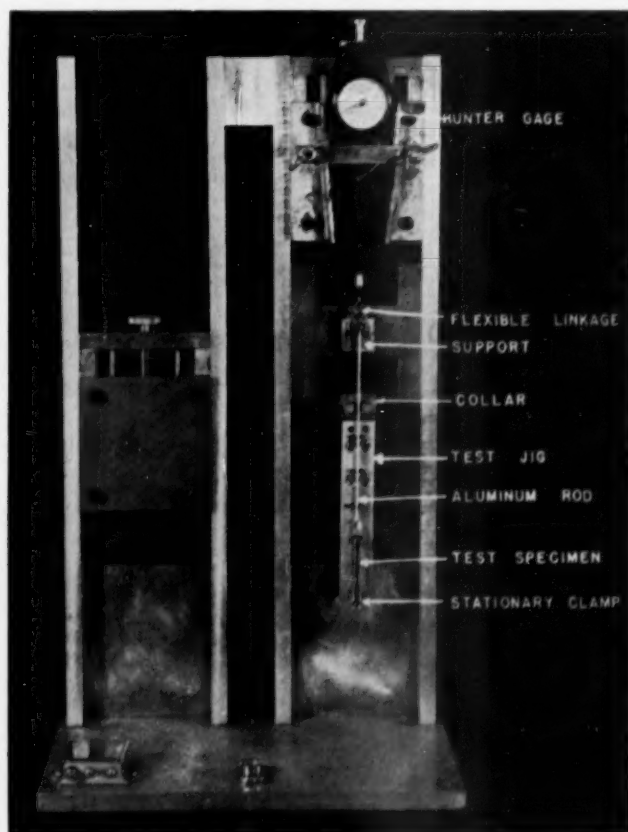


FIG. 2.—Tensile stress relaxation apparatus.

subjected to the required aging conditions. The load reading on the gauge, minus the weight of the aluminum rod and the specimen, is equal to the back force exerted by the elongated specimen.

PROCEDURE

In operation, one end of a T-50 specimen is hooked onto the stationary clamp and the other end onto the aluminum rod. The specimen is then elongated within 5 seconds to the desired elongation. At 3 minutes (± 10 seconds) after elongation, the back force is determined. The assembled test jig is then removed from the apparatus and permitted to condition for 60 (± 5) minutes at room temperature prior to aging. When the test jig has been aged at elevated temperature, the assembly is allowed to cool for 60 (± 5) minutes at room temperature before the test. Except for the time spent in obtaining readings of the back force, the assembled test jig was stored and aged in a cellulosic enclosure to minimize ozone effects. This precaution was taken because ozone affects rubber materials more in tension than in compression.

TEST RESULTS

For stress relaxation in compression and in tension, the following calculations were made:

$$\text{Back stress (lb. per sq. in.)} = \frac{\text{back force exerted by specimen}}{\text{cross-sectional area of specimen}}$$

Stress relaxation (per cent)

$$= \frac{\text{back stress in unaged specimen} - \text{back stress in aged specimen}}{\text{back stress in unaged specimen}} \times 100$$

The specimens used for this investigation were a GR-S stock compounded to meet the requirements of Military Specification MIL-R-900A and a Butyl stock that was assumed to have high stress relaxation. The recipes and initial physical properties of these stocks are given in Table I.

TABLE I
RECIPES AND PHYSICAL PROPERTIES OF RUBBER STOCKS

GR-S stock		Butyl stock	
GR-S	100.0	GR-I	100.0
Zinc oxide	5.0	Zinc oxide	5.0
Philblack-A	40.0	Stearic acid	3.0
Heliobone	1.0	Philblack-A	30.0
Flexol-TOF	20.0	Circel L.F. oil	10.0
Methyl Tuads	0.8	Tuads	1.0
Sulfur	1.0	Captax	0.5
		Polyac	1.0
		Sulfur	2.0
Cure for 1-in. thickness: 22 min. at 310° F		Cure for 1-in. thickness: 35 min. at 310° F	
Tensile strength (lb. per sq. in.)	1390	Tensile strength (lb. per sq. in.)	1950
Elongation (per cent)	460	Elongation (per cent)	585
Hardness (Shore A)	45	Hardness (Shore A)	40

Tests were made to determine the relationship between stress relaxation in compression and in tension with respect to percentage of deformation. The test-specimens, prepared from the GR-S and Butyl slabs, were deformed 10, 20, and 30 per cent in compression and 20, 40, 60, and 80 per cent in tension. After the initial back force readings were obtained, the deformed specimens

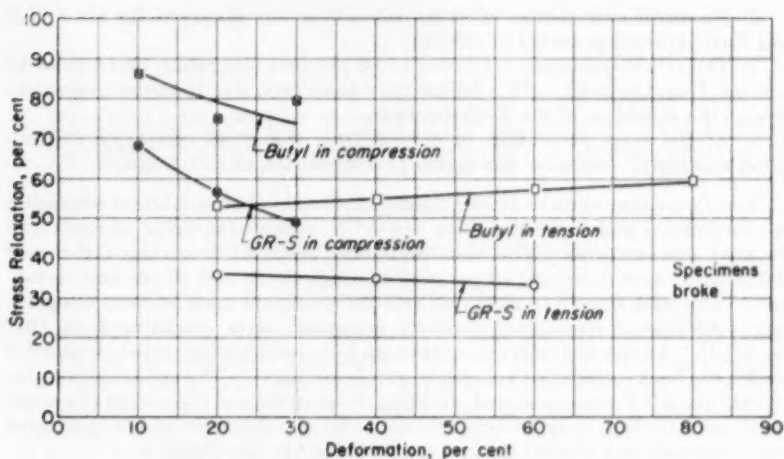


FIG. 3.—Stress relaxation in compression and tension vs. deformation. Specimens aged for 46 hours at $194^{\circ} (\pm 2^{\circ})$ F.

were conditioned for 46 hours at $194^{\circ} (\pm 2^{\circ})$ F. Following this aging period, the back force in the specimens was again determined. Stress relaxation was calculated and plotted against per cent deformation in Figure 3.

From Figure 3 it can be seen that:

1. The stress relaxation in compression of both GR-S and Butyl specimens decreased with increase of deformation. Stress relaxation in compression for Butyl at 20 per cent deformation was lower than for 10 or 30 per cent deformation. However, additional data are necessary to determine the exact shape of this curve.

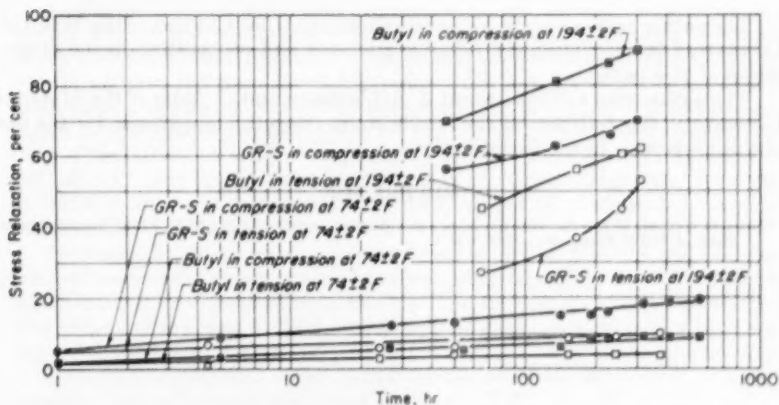


FIG. 4.—Stress relaxation in compression and tension vs. time. Specimens subjected to continuous aging at room temperature and at $194^{\circ} (\pm 2^{\circ})$ F. Compression tests conducted at 20 per cent deformation; tension tests at 40 per cent deformation.

2. No significant change of stress relaxation was observed for the GR-S and Butyl specimens tested in tension.

3. The GR-S specimens subjected to 80 per cent elongation broke prior to removal from the oven. This failure may have been due to stress concentration at the shoulders of the T-50 specimen.

4. At the same percentage of deformation, the stress relaxation of both GR-S and Butyl specimens was higher in compression than in tension.

Tests were also made to determine the relationship between stress relaxation in compression and in tension with respect to continuous aging at room and elevated temperatures. The test-specimens, prepared from the GR-S and Butyl slabs, were deformed 20 per cent in compression and 40 per cent in tension. The back force was measured and the specimens aged at room temperature. Additional specimens, similarly deformed, were conditioned at $194^{\circ} (\pm 2^{\circ})$ F. At selected intervals of time up to a conditioning period of about 2 weeks, the back force in the specimens was determined. The conditioning time at $194^{\circ} (\pm 2^{\circ})$ F was calculated, omitting those periods of time when the specimens were cooling to room temperature. Stress relaxation of the specimens was calculated and plotted against conditioning time in Figure 4.

From Figure 4 it can be seen that:

1. The stress relaxation of both GR-S and Butyl in compression and in tension increased with aging time and temperature. Conditioning the specimens at $194^{\circ} (\pm 2^{\circ})$ F greatly increased the stress relaxation of both the GR-S and Butyl specimens.

2. The Butyl specimens exhibited higher stress relaxation at $194^{\circ} (\pm 2^{\circ})$ F in both compression and tension than the GR-S specimens, whereas at room temperature the reverse was true. The Material Laboratory is unable to give a reason, at present, for this apparent reversal in expected results.

3. Plotting the data on semilogarithmic paper appears to be a convenient way to correlate the effects of room temperature aging with accelerated aging conditions.

ACKNOWLEDGMENTS

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The author also wishes to thank J. Z. Lichtman and G. Alder of the Material Laboratory, the designers of the tensile stress relaxation apparatus, for the use of this apparatus in the investigation.

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A COMPARISON OF THE FLOW OF HIGH POLYMERS IN THE CAVITY OF A MOONEY PLASTOMETER *

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INTRODUCTION

In 1951 a brief survey of the viscosity-time curves obtained during the shearing of GR-S and Butyl synthetic rubber samples in a Mooney plastometer was made¹. As a result, some views on the flow inside the cavity of this plastometer have been formed, and the work described below is a continuation of the original study. Two comparisons have been attempted: the comparison of the flow curves of high polymers whose structure and properties were either measured or known, and the comparison of the actual rubber residues taken from the machine after shearing.

IDEALIZED MOONEY CURVES

When a high polymer is sheared under standard conditions in a Mooney plastometer, the strain on the shearing mechanism is measured and can be plotted against time². It has been the custom for the rubber industry to depend chiefly on the Mooney value, i.e., the measured strain, after four minutes' shearing, but in previous work it was suggested that all parts of the curve may reflect the structure of the sample¹.

Two very important types of synthetic rubber, Butyl and GR-S, were found to give two distinct types of Mooney curves. Idealized curves for these two rubber types are given in Figures 1 and 2.

In Figure 1, which is for Butyl rubber, a steady flow portion A'C' or BC is shown, but the dotted-line curve A'C' has the characteristic shape for samples which have been heavily "massed", i.e., milled between heated rolls, and cooled, but which have not been allowed to relax in the hot cavity of the machine for more than a second or two. The full line, ABC, is typical of a low-viscosity Butyl sample relaxed or conditioned for the normal period of one minute. The part of the curve OA (or OA') was largely the result of rubber extension, while AC (or A'C') was largely due to flow of rubber. When a high-viscosity sample of Butyl rubber was tested, with the usual period of conditioning, the curve followed the shape OABA'C'.

In Figure 2 the curves are shown of two typical GR-S rubbers, i.e., butadiene-styrene copolymers, which have not been massed prior to running, but which have been conditioned in the machine for one minute before shearing. The difference in shape of these curves may be seen in comparison with those of Figure 1: the low and flattened part of the curve OA and the secondary rise at C in about four minutes. The sample giving curve OABC would be lower in viscosity and gel content than that giving OA'B'C'.

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MOONEY CURVES OF VARIOUS HIGH POLYMER TYPES

Some ten distinctive types of high polymer relating to Butyl or GR-S synthetic rubber were run in a standard Mooney machine at 212° F. A standard rotor was used, and the rotor speed was kept at 2 r.p.m. according to the requirements of one of the commonest tests carried out by this machine³. Each high polymer was allowed to condition in the machine for one minute (unless stated to the contrary), and according to thermocouple measurements made in the sample mass inside the cavity, the high polymer temperature at the start of shear was within 5° of 212° F.

While there is no reason to think that the curves shown in Figures 3-10 are the only ones which might be obtained for their polymer group, in most cases the main shape of the curve would seem to be characteristic of typical samples.

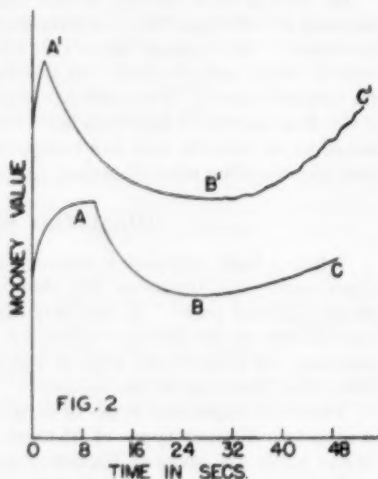
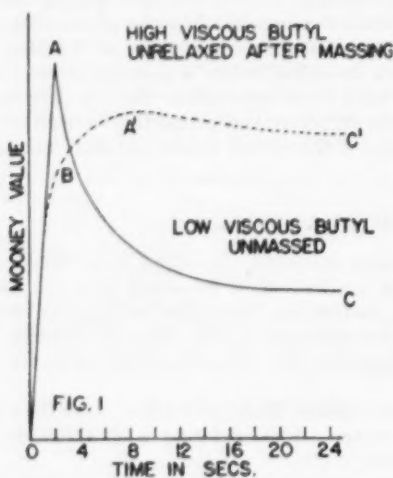


FIG. 1.—Idealized Mooney plasticity-time curves for Butyl rubbers.

FIG. 2.—Typical Mooney curves of unmassed butadiene-styrene copolymers containing about 23% bound styrene.

Where duplicate runs were made (not done in the case of polystyrene, the natural rubbers, or "special" rubbers) the curves lay within two Mooney points of each other at comparable times.

All samples were run between cellophane sheets to prevent the polymer from sticking to the rotor or platens.

Some properties of the miscellaneous polymers are listed in Table I, the butadiene-styrene (or related) copolymers in Table II, and the Butyl samples selected as typical in Table III.

Intrinsic viscosities, $[\eta]$, and the branching factor, k' , were both found from measurements of dilute solution of polymer in toluene³. The solutions were filtered to remove gel and then run in an Ubbelohde viscometer at 25.0° C ($\pm 0.02^\circ$). Concentrations were kept below 0.5 g. per 100 ml., and k' was calculated from the slopes of the viscosity curve, using the relation:

$$(\ln \eta_r)/c = [\eta] - \beta[\eta]^2 c$$

and

$$k' = (0.50 - \beta)$$

where η_r is the relative viscosity, c is concentration, and $\beta[\eta]^2$ is the slope of the curve.

The gel content of polymers was obtained by suspending a 0.1-gram sample of polymer within a 100-mesh stainless steel wire cage in toluene at room tem-

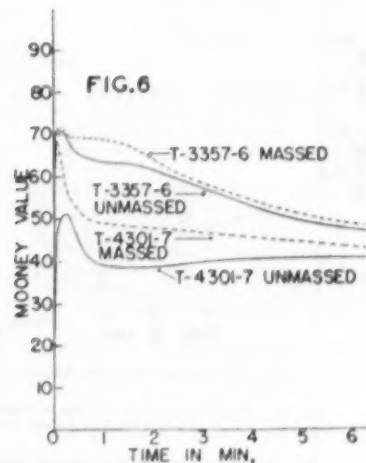
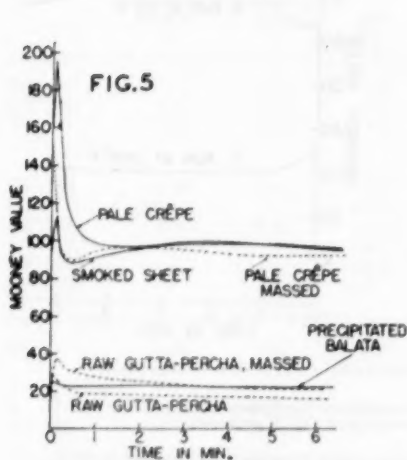
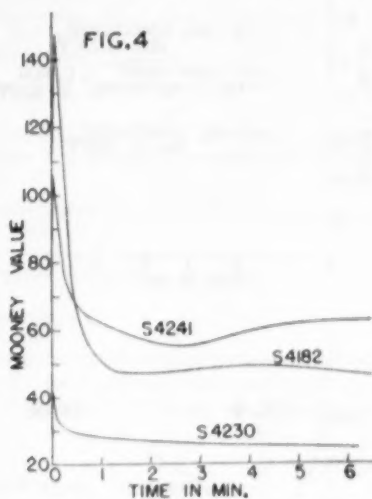
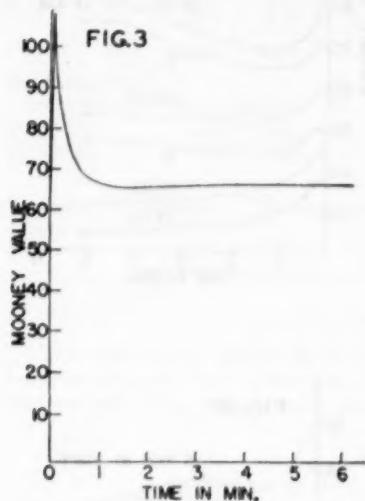


FIG. 3.—Mooney curve of a sample of polystyrene run at 273° F.

FIG. 4.—Mooney curves of samples of polyisobutylene run at 212° F.

FIG. 5.—Mooney curves of Natural rubber samples run at 212° F.

FIG. 6.—Mooney curves of samples of polybutadiene (polymerised at 122° F) run at 212° F.

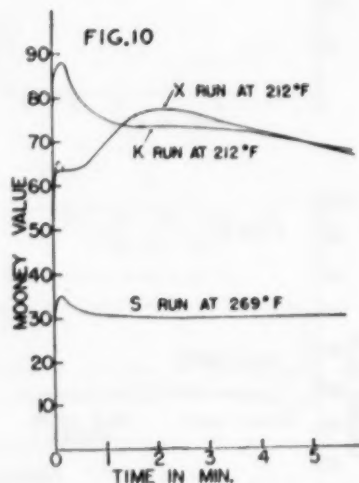
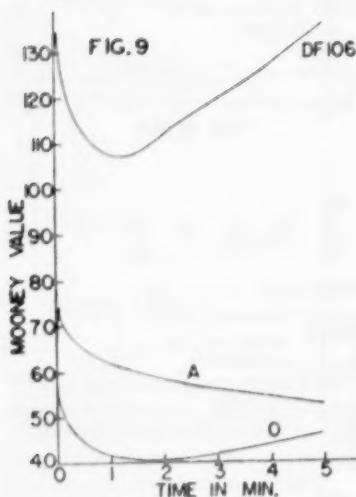
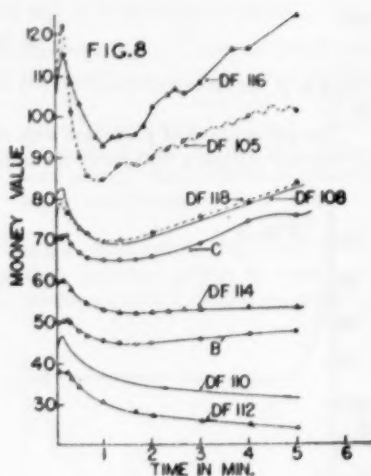
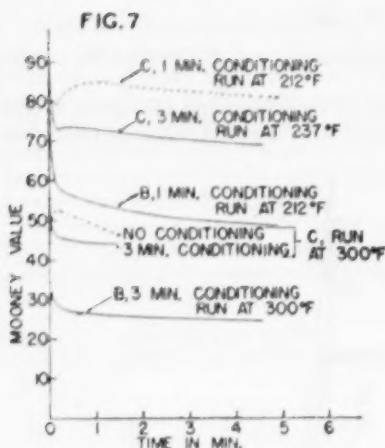


FIG. 7.—Mooney curves of samples of Butyl rubber, run at various temperatures.

FIG. 8.—Mooney curves of samples of butadiene-styrene copolymers (polymerized at 122° F and with 23% bound styrene) run at 212° F unmassed.

FIG. 9.—Mooney curves of samples of butadiene-styrene copolymers (polymerized at 55° F and with 23% bound styrene) run at 212° F unmassed.

FIG. 10.—Mooney curves of samples of miscellaneous synthetic rubbers polymerized at 122° F. and run at various temperatures. Sample X was a butadiene-styrene copolymer with 25% bound styrene and 0.3% divinylbenzene. Sample S was a butadiene-styrene copolymer with 85% bound styrene. Sample K was a butadiene-acrylonitrile copolymer with 32% bound acrylonitrile.

TABLE I
PROPERTIES OF POLYMERS

	Intrinsic viscosity (η)	Branching factor (k')	Gel (%)	Comments
Polystyrene	1.18	0.33	—	Preheated to 280° F before the Mooney run
Polyisobutylene				
S.4230	0.92	0.38	—	Conversion 51%
S.4241	2.51	0.37	—	Conversion 52%; after Mooney run [η] = 2.51
S.4182	5.06	0.39	—	Conversion 72%
Polybutadiene, polymerized in emulsion at 122° F				
T-4301-7	2.03	0.43	—	After Mooney run [η] = 2.02, k' = 0.41
T-3357-6	2.25	0.39	—	After Mooney run [η] = 2.19, k' = 0.35

perature for 48 hours. The cage and residue were dried at 100° C for one hour before weighing.

THE COMPARISON OF ACTUAL MOONEY CURVES

(A) PRIMARY PEAKS

The outstanding feature of the Mooney curves of polystyrene and polyisobutylene, Figures 3 and 4, was the extremely sharp primary peak reached within four seconds from the start of shear. The curves of these two types were

TABLE II
PROPERTIES OF BUTADIENE-STYRENE COPOLYMERS

	Intrinsic viscosity (η)	Branching factor (k')	Gel (%)	Comments
<i>Polymerized in emulsion at 122° F, 23% bound styrene</i>				
DF.112	1.50	0.36	0.7	Pilot plant batch, 62% conversion
DF.110	1.82	0.35	0.2	Pilot plant batch, 57% conversion
B	2.37	0.42	1.2	Plant batch, 72% conversion; after Mooney run [η] = 2.37, k' = .40
DF.114	2.20	0.34	1.0	Pilot plant batch, 59% conversion
C	>3	—	61.2	Plant batch, 73% conversion
DF.108	2.96	0.35	14.5	Pilot plant batch, 59% conversion
DF.118	—	—	36	Pilot plant batch, 60% conversion
DF.105	—	—	58.6	Plant batch, 71% conversion
DF.116	—	—	47	Pilot plant batch, 59% conversion
<i>Polymerized in emulsion at 55° F, 23% bound styrene</i>				
O	3.89	0.37	5.7	Supposed to be identical with DF.106 coagulated with 45 oil: 100 polymer. Analysis based on oil-free sample
A	2.17	0.32	0.1	
DF.106	3.78	0.36	40.8	Plant masterbatch, 70% conversion
<i>Polymerized in emulsion at 122° F, miscellaneous types</i>				
S	1.21	0.34	10.0	85% bound styrene
X	—	—	78.2	25% bound styrene + 0.3% divinyl- benzene
K	—	—	39.7	32% acrylonitrile replacing all styrene

similar in general shape to that of a typical low-viscosity Butyl rubber with a low branching factor (see Butyl-B, Figure 7), but very different in shape from the curves of polybutadiene (Figure 6). The primary peak of the polybutadiene curves for unmassed samples was not at all sharp, and was not reached until 10-17 seconds after shearing was started.

A further set of natural rubber samples was then run (Figure 5). Raw pale crepe rubber, which is considered to be fairly pure polyisoprene polymerized without branches in a latex emulsion in the Hevea tree, showed a sharp primary peak rather similar to polyisobutylene. This sample would probably have been rolled at least once. Smoked crepe, a less pure grade of latex dried under conditions which might be expected to lead to more cross-linking, showed a broader peak than raw pale crepe. Balata gum, precipitated and purified, showed a sharp primary peak in spite of its low viscosity at 212° F, but the Gutta-percha sample, which contained some gums and resins other than pure rubber, showed again a flattened peak. These tests, though too few to be conclusive, suggested that the sharpness of the primary peak might be related to lack of branching in a polymer, or to some similar structural feature of the material, rather than to the process of manufacture.

TABLE III
PROPERTIES OF BUTYL RUBBER SAMPLES CONTAINING ABOUT 8 PER CENT
ISOPRENE COPOLYMERIZED WITH ISOBUTYLENE

	Intrinsic viscosity (η)	Branching factor (k')	Gel (%)	Comments
B	1.10	0.37	0.1	After Mooney run $[\eta] = 1.03$, $k' = .36$
C	1.30	0.40	1.3	After Mooney run $[\eta] = 1.28$, $k' = .39$

(B) SECONDARY PEAKS

It will be noticed from Figures 1 and 2 that, in addition to the primary peak, a secondary rise may also appear in certain Mooney curves. In Butyl rubber samples, this secondary rise occurred within one minute of the start of shearing, and was dependent on the temperature of the sample. Thus a sample which showed a pronounced secondary rise (Butyl C, Figure 7) when run at 212° F after one minute of conditioning showed less rise if the conditioning period were extended or if the temperature were raised. Low-viscosity samples showed even less rise, or none whatever.

With GR-S samples and related rubbers, the secondary rise was also noticeable. However, with these materials it was seldom noticeable until after one and one-half minutes of shearing, and often did not attain its peak until some four or five minutes had elapsed. With these rubbers the secondary rise was hardly affected by temperature change or conditioning period, but was certainly increased by increasing molecular weight and increasing gel as Figure 8 and Table II show.

COMPARISON OF PLUGS OF ACTUAL MOONEY SAMPLES

To determine the particular reasons for these flow peculiarities, several experiments were devised. Samples of GR-S and Butyl rubber were evacuated for 24 hours at 100° C, at a pressure around 10 mm. mercury. Nitrogen was then admitted at atmospheric pressure, and the samples were allowed to cool in its atmosphere before they were run in the Mooney machine. Since no appreciable change in the flow curve resulted, it was concluded that entrapped air played little part in influencing the shape of the flow curves.

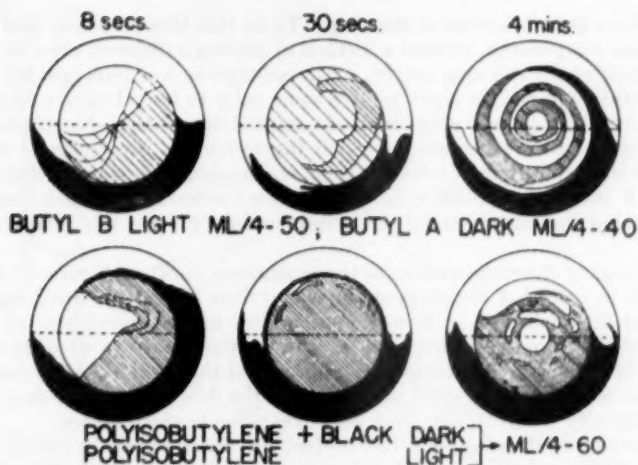


Fig. 11.—Drawings of cross-sections of actual sample plugs from the Mooney machine: Butyl (low viscosity) and polyisobutylene after 8 seconds, 30 seconds, and 4 minutes shearing (i.e., one quarter, one, and eight revolutions).

A study of the decay of stress in the sample after shearing, but while the sample was still in the machine, was a little more useful. This indicated that no true structural effect occurred in Butyl rubbers to cause the secondary rise, but in GR-S samples a lasting change occurred in the sample during its shearing.

Greatest progress was made by examining the sample plugs from the ma-

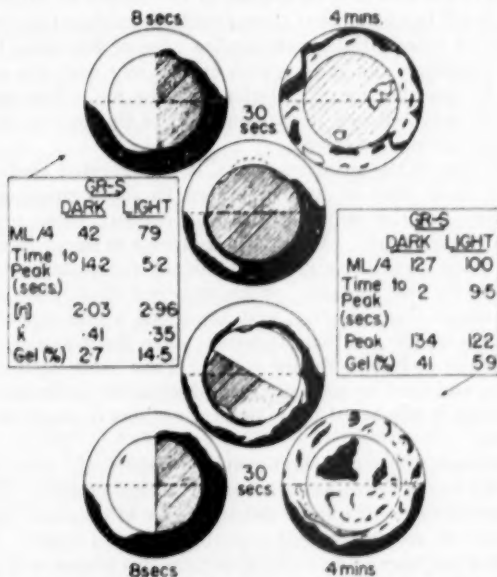


Fig. 12.—Drawings of cross-sections of actual sample plugs from the Mooney machine: GR-S (i.e., butadiene-styrene copolymers with 23% bound styrene) of low and high viscosity after 8 seconds, 30 seconds, and 4 minutes shearing.

chine after a definite period of shearing. To do this Messrs. Storey and Briggs of Polymer Corporation devised a method of placing a different color of rubber in each half of the shearing cavity. Polyisobutylene was impregnated with a small quantity of carbon black to give some color to it. However, the GR-S samples had to be colored with chemicals, since milling with carbon black would destroy the original structure on which the secondary rise seems to depend. After it had been run for the desired time, the machine was stopped and heated to 300° F in order to allow a fairly permanent relaxation of each sample to occur so that the sample would not distort unduly when it was removed from the die.

Drawings of the cross-sections of these plugs are shown in Figures 11 and 12.

It will be seen that the plugs of polyisobutylene indicate a stretching of the sample at first, followed by flow of a streamline nature, which started at the outside of the rotor. As time went on, the sample seemed to wind up around the axis of shear and the streamlines approached the center. After four minutes there was some indication of breakup in the flow units. The flow planes of low viscosity Butyl rubber were also streamline in their nature.

In the case of the plugs of GR-S rubber, extension was again visible, but to a much smaller extent than in Butyl or polyisobutylene. With the extension was definite evidence of slippage along certain slip planes at fixed distance from the center. This, apparently, was the cause of flatness in the primary peak which has been noted above. After about 30 seconds of shearing, the GR-S samples showed signs of a peculiar turbulence or nodulizing, which became more and more apparent with time. This coincided with the period of "secondary rise".

DISCUSSION OF RESULTS

If these results are accepted as typical of the classes of rubber from which they are taken, it will be agreed that these synthetic rubbers fall into two classes: those which exhibit substantially a streamline type of flow after high extension in the Mooney chamber, and those which exhibit slip with the primary extensions, followed by granulation or turbulence in the main flow section. These two forms of flow may be used to explain most of the curves obtained during the survey of the various polymers.

On consideration of the primary peaks, it is suggested that emulsion-produced polymers have lines of low resistance to shear running between the emulsion granules. If the polymer has been massed, these granules will be broken open to some extent. Also, if the polymer is linear in structure, it is suggested that there would be a greater tendency for granules to become uniformly interlinked by heat motion. With branched chains, the granules would more probably retain their identity, and hence one would expect a greater extension of slippage on the original extension, since the granules would only be intertangled by free ends of polymer chain. That some such correlation between branching and time to primary peak does occur is shown by Figure 13, in which branching is measured by k' determinations from dilute solution viscosity in toluene.

As flow continues, these emulsion granules apparently tend to form larger aggregations, which give the appearance of turbulence of flow. The turbulence is not in this case precisely the same as turbulence of ordinary liquids, and the Reynold's number as ordinarily used probably does not apply. However, the tendency of GR-S polymer to flow along certain slip planes will raise the relative velocity of different parts of the sample to high local values and increase

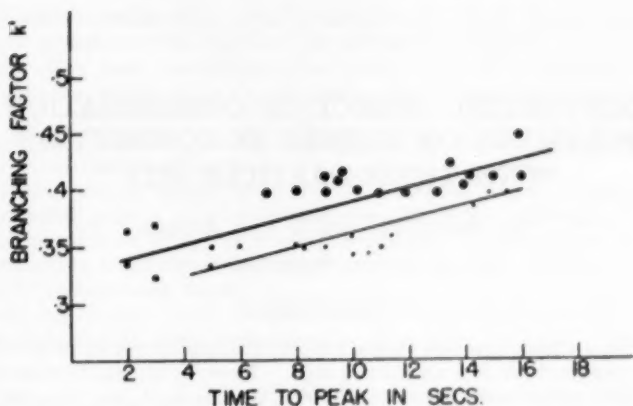


Fig. 13.—The variation between the branching factor k' and the time to reach Mooney peak. The upper line is for plant samples, the lower line for pilot plant batches. All samples were butadiene-styrene copolymers with 23% bound styrene. The square points indicate samples polymerized at 55° F; all others were polymerized at 122° F.

the granular appearance which results. It is also suggested that increased branching or entanglement (looping of chains) will increase the apparent turbulence and so give a greater secondary rise to the shearing force. This is borne out by Figure 8, in which the secondary rise clearly increases with the increase in molecular weight (and gel content) of the polymer.

SUMMARY

From idealized Mooney plasticity-time curves for Butyl and GR-S synthetic rubber, the distinctive features of the various parts of the shearing curve are pointed out. Actual experimental curves are given for Butyl, GR-S, "cold rubber", polyisobutylene, polybutadiene, polystyrene, and some natural-rubber gum stocks. For polymers which were produced in emulsion, the degree of branching as indicated by the Huggins k' value seemed to be loosely correlated with the time to reach the primary peak in the Mooney flow curve. Cross-linking and entanglement in structure as indicated by high gel content seemed to be correlated with secondary rise in shearing force shown during a long test. An hypothesis of flow in the cavity of the Mooney machine is advanced to explain these phenomena, supported by drawings of cross-sections of samples run in the machine. According to this hypothesis, some high polymers shear in a streamline fashion, others shear along certain slip planes and may even exhibit a mixing of parts which seems to be similar to turbulence in fluids.

ACKNOWLEDGMENT

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REINFORCING EFFECT OF CONDENSATION POLYMERS ON RUBBER IN CONNECTION WITH THEIR PARTICLE SIZE *

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INTRODUCTION

It is still an open question to what extent the reinforcing effect of a filler in rubber is due to physical or chemical bonds. There is abundant evidence¹ that the reinforcing effect with regard to modulus, tear strength, and abrasion resistance increases with decreasing particle size. Arguments have been brought forward², however, that below a certain particle size this reinforcing effect diminishes. In most of the experiments involved, carbon black has been used as a filler. In the present paper, data regarding the reinforcing effect of some condensation resins of different particle size are presented in order to bring more light on these questions.

CONDENSATION POLYMERS AS REINFORCING FILLERS FOR RUBBER

It has often been tried to combine synthetic resins, especially phenolformaldehyde resin, with rubber³, but the results have not been encouraging⁴ except with the acrylonitrile-butadiene polymers⁴. The formation of the resin in the rubber⁵ leads to more promising results.

The formation of condensation polymers in latex has been investigated⁶, a process which has had most success in the hands of Le Bras and Piccini⁷, who reinforced objects directly prepared from latex by the formation of resorcinol-formaldehyde resin in latex.

Van Alphen has shown that aminoplasts (aniline resin, melamine resin, urea resin) can easily be formed in stabilized latex by proper addition of the components of the condensation resin⁸. For example, for the aniline resin compounds, latex is stabilized with a nonionic stabilizer. By adding HCl-aniline and formaldehyde, the whole mass, including the rubber, gels. It is neutralized with ammonia, washed, and dried.

In this way products containing 0-100 per cent resin (calculated on total resin + rubber) can be prepared. As long as the resin content is between 0 and 70 per cent, they can be worked on the mill and vulcanized like dry rubber. With a resin content between 0 and 30 per cent, the finished products are highly elastic and rubberlike, getting increasingly tough and leatherlike with more resin; with 60-70 per cent resin they become hard and breakable.

THE REINFORCING EFFECT

The use of the term "reinforcing" in rubber science is very confusing, and it is necessary to name exactly the specific property which is being enhanced.

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Thus phenolic resins when mixed in natural rubber according to the method of Dunlop⁹ do enhance the modulus, but not the tear resistance¹⁰.

On the other hand, resorcinol-formaldehyde resin when prepared in latex according to the method of Le Bras-Piccini⁷ enhances not only the modulus but also the tear strength of the rubber films. This reinforcement disappears for the greater part, however, when the rubber is deformed; the reinforced rubber shows a pronounced Mullins effect¹¹.

As already stated, aniline resin, and to a smaller extent melamine resin, when condensed in latex, enhance the modulus and the tear resistance of the dry rubber prepared from latex and worked on the mill. Figures 1 and 2 present these reinforcing actions, the Mullins effect in these cases being of the same order as for carbon-black mixtures.

Reinforcing carbon blacks are known to have a particle dimension of 20–40 μ (200–400 Å) and, when well dispersed, they are thus submicroscopically

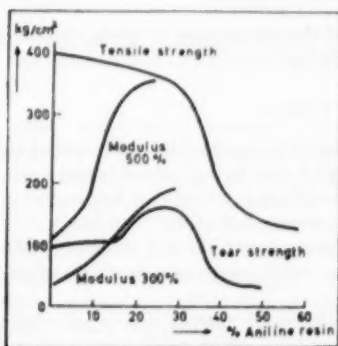


FIG. 1.—Technical properties of natural rubber-aniline resin compositions.

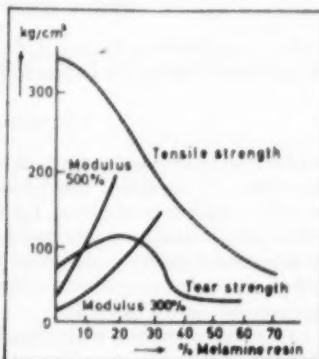


FIG. 2.—Technical properties of natural rubber-melamine resin compositions.

divided in the rubber. The connection between the particle diameter of the filler and the reinforcement of rubber is generally appreciated¹².

Certain authors have come to the conclusion that a small amount of strong primary linkages between the rubber and the carbon black is also essential¹³. These linkages may be formed on mastication or on vulcanization. But then reinforcement must be a function of the total surface and of the number of primary linkages per unit of surface. It can then be thought that a filler with a greater number of primary linkages per unit of surface (e.g., a resin) can be used in a coarser form than one in which this concentration of primary linkages is less (e.g., carbon black), resulting, however, in the same reinforcing effect.

Blanchard¹³, who also accepts that a relatively small number of strong linkages induced by carbon black particles are an important factor in the reinforcement of rubber by carbon blacks, states explicitly: "For a given dispersion and concentration of filler, it is suggested that reinforcement is most likely to find proper expression in terms of the number of particles and the number of linkages per particle, both factors being functions of the particle size. One consequence of this theory is a limit to the advantage which can be obtained by using smaller particles."

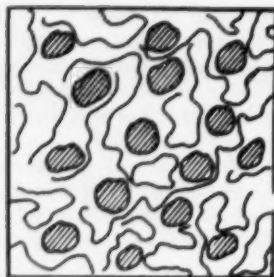


FIG. 3.—Heterogeneous mixture of rubber and cyclized rubber (milled).



FIG. 4.—Homogeneous mixture (partially cyclized rubber).

RESIN REINFORCEMENT

The above suggestion about a limit of the advantage of using smaller particles was confirmed for resins in the following way.

CYCLIZED RUBBER

When natural rubber in the form of latex is treated with concentrated sulfuric acid, the rubber is cyclized, the latex globules being transformed into resin particles with a diameter of about $1\ \mu$ ($= 10^4$ A.), which can be used as a reinforcing filler (regarding modulus and hardness) in ordinary rubber¹⁴.

A rubber reinforced by addition of this cyclorubber will present, after milling, a rather coarse heterogeneous mixture containing resin particles of presumably $1\ \mu$ diameter (see Figure 3).

One can make a rubber with about the same (total) degree of cyclization from latex by partly cyclizing the rubber by a short treatment with sulfuric acid¹⁴. Since this product cannot be separated in different fractions, we must assume that the molecules of the rubber themselves have partly been mutually

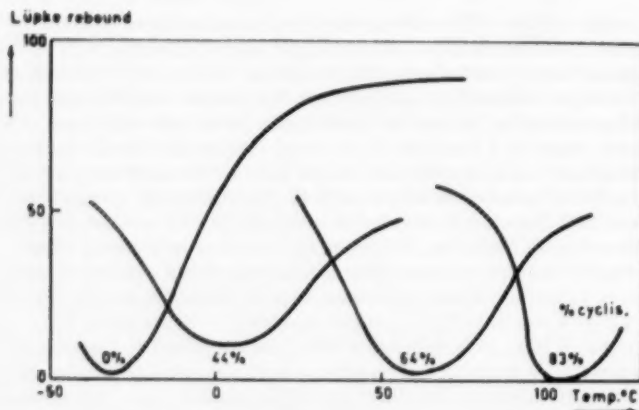


FIG. 5.—Rebound-temperature functions of natural rubber and three cyclized rubbers prepared from latex.

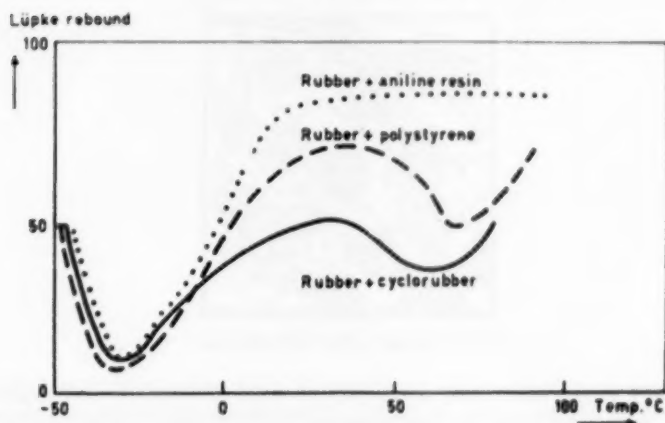


FIG. 6.—Rebound-temperature curve: for 100/50 compounds of rubber and cyclized rubber (full line), of rubber and high styrene resin (dashed line) and for an 80/20 compound of rubber and aniline resin (dotted line).

interlinked during the cyclization process; they will presumably consist of uncyclized parts of the chains and cyclized parts as presented by Figure 4; some of the cyclized parts may act as the interlinking bridges. We will call this a homogeneous distribution (homogeneous on a molecular scale).

A confirmation of these theories concerning the structures of these products is obtained, when plotting the rebound elasticity (Lupke resilience) against temperature for both products.

As can be seen from Figure 5, natural rubber has only one minimum in the rebound, namely, at -31°C , and on cyclizing the rubber according to Figure 4, this minimum shifts to higher temperatures.

If, however, one makes a heterogeneous mixture of rubber according to Figure 3, this mixture shows two minima (Figure 6). The same applies to a mixture of rubber and polystyrene resin¹⁵. Each minimum presumably corresponds to certain physical changes in one of the components.

Thus it is felt that the heterogeneous compound can be described as consisting of relatively large resin particles of, say, 10^4 \AA diameter embedded in the rubber macromolecules with a diameter of 5 \AA and a length of about $2 \cdot 10^4 \text{ \AA}$ (for a molecular weight of 350,000).

TABLE I
COMPARISON OF THREE VULCANIZED RUBBERS

Test	Heterogeneous mixt. with 20% cyclized rubber (Figure 3)	Homogeneous mixt. (Figure 4), degree of cyclization 22.5%	Unreinforced rubber (for comparison)
Modulus at 300% (kg./cm. ²)	80	24	19
Tensile strength (kg./cm. ²)	286	26	321
Elongation at break (%)	564	325	780
Tear strength, Delft method (kg./cm. ²)	82	13	57
Hardness (Shore A)	56	45	30
Elasticity (Shore)	90	52	93

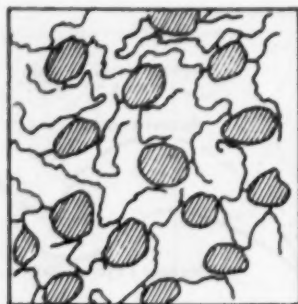


FIG. 7.—Rubber aniline resin compound.

Table I shows that, from a mechanical point of view, the heterogeneous mixture is preferable to the homogeneous partly cyclized rubber mixture, a point which could hardly be predicted, but which confirms Blanchard's theory that the size of the reinforcing particles shall surpass a minimum.

ANILINE RESINS

For reinforcing resins like aniline resin, prepared in latex, there are reasons to assume that these resin particles are bound to the rubber molecules by chemical bonds, although of course there will be no stoichiometric relation between the resin and the rubber.

One of the reasons is that rubber in latex can react with formaldehyde in hydrochloric acid¹⁶. The formation of bridges between the aniline resin and the rubber molecules by means of the formaldehyde molecules already bound to the rubber is very plausible, since the rubber can no longer be extracted from the unvulcanized product (gel formation). Schematically such a rubber-resin compound can be presented by Figure 7.

When this heterogeneous resin-rubber compound is plasticized, about half of the rubber can be extracted from a material originally containing 30 per cent resin (Figure 8). This leads to the assumption that part of the rubber is torn off from the resin (Figure 9) during the mastication process. That the remaining gel content of the plasticized rubber is not due to an inclusion of the rubber in "cages" of resin follows from the observation that, from a plasticized rubber-

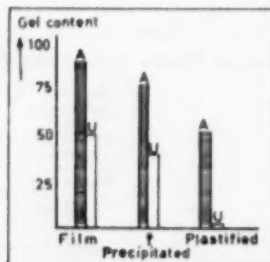


FIG. 8.—Gel content (benzene extraction) of unvulcanized rubber containing 30 per cent of resins: (A) = aniline-formaldehyde resin; (U) = urea-formaldehyde resin.

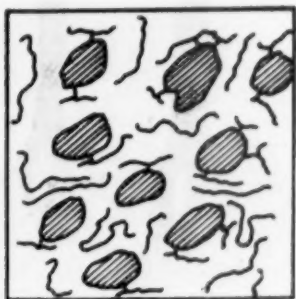


Fig. 9.—Rubber-aniline resin compound (plasticized).

urea-resin compound prepared in the same way as an aniline resin compound, nearly all the rubber can be extracted (Figure 8). As a matter of fact, urea resin does not reinforce rubber as well as aniline resin does¹⁷, and this is a confirmation of the theory that chemical bonds can help¹⁸ in creating a reinforcing effect (it has still not yet been proved that chemical bonds are necessary for producing reinforcement, as claimed by Stearns and Johnson¹²).

A further argument in favor of the binding of rubber to the aniline resin is found in the fact that the latter, when prepared in stabilized latex, precipitates the latex: even the formation of as small an amount as 0.5 per cent aniline resin in 60 per cent latex stabilized with Emulphor-O precipitates the rubber completely.

During the formation of the resin in the aqueous phase of the latex, it is supposed to build up a somewhat cagelike structure, something like presented in detail by Figure 10. These resin particles are relatively large and can be seen by means of an ordinary microscope (Figure 11)¹⁹. It can be understood that this rigid structure reinforces latex films (compare resorcinol-formaldehyde resin), but once this structure has been broken by deformations, a large part of the reinforcement will disappear irreversibly.

There is evidence that, after breaking such a structure, parts of it will be orientated in the direction of stretching, causing anisotropy (Figure 12).

After plasticizing on the mill, the structure will be broken completely, and it will then not be mainly the shape of the resin particles which determines the properties of the compound, but the properties of the particles themselves, e.g., their hardness. This is shown by plotting the mechanical loss factor δ (measure

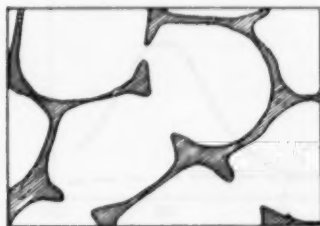


Fig. 10.—Schematic picture of a latex film containing 10 per cent resorcinol-formaldehyde resin. $\frac{3}{4}$ inch = 1000 μ .



Fig. 11.—Latex film containing 30 per cent aniline resin dyed with iodine in benzene. $\frac{5}{8}$ inch = 10 μ .

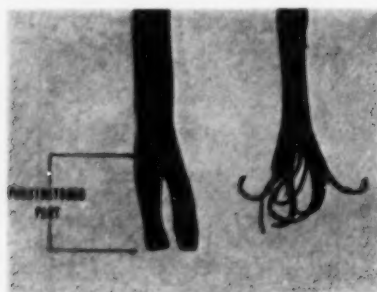


FIG. 12.—Latex film with 20 per cent resorcinol-formaldehyde resin prestretched and torn by hand.

for hysteresis losses on vibration) vs. temperature for natural rubber containing aniline resin (plasticized on the mill) and a similar mixture, containing polystyrene resin (Figure 13)³⁰.

The curve of the polystyrene mixture shows a peak at about 80° C, coinciding with the minima in the temperature rebound curves of polystyrene resin-rubber and cyclized rubber-rubber compounds (Figure 6). This peak in the $\tan \delta$ -temperature curve and the corresponding minima in the temperature-rebound curves are ascribed to the fact that polystyrene resin and also cyclized rubber are thermoplastic materials, passing their second-order transition point at this temperature, contrary to aniline resin, which does not soften at temperatures below 300° C.

That reinforcement of rubber by resins is connected with the hardness of the resin particles follows from the experimental fact that, by lowering the hardness of the aniline resin, the reinforcing effect with regard to the modulus or the hardness also diminishes. This lowering of the hardness can be brought

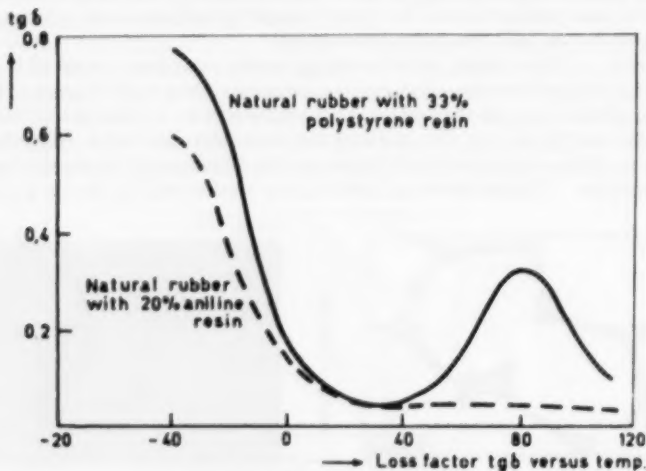


FIG. 13.—Loss factor $\tan \delta$ vs. temperature.

about by using less than 1.5 mole formaldehyde on 1 mole aniline in the preparation, giving products softening at lower temperatures²¹ or by replacing part of the whole of the aniline by para-substituted anilines as *p*-toluidine or *p*-tert-butylaniline. In both cases the reinforcing effect diminishes.

That, on the other hand, the reinforcing effect can also be connected with the formation of chemical bonds can be proved by adding the hard thermo-setting material: urea resin. When prepared in latex, its reinforcing properties on rubber are fairly poor. (Modulus at 300% elongation of 30% urea-resin-rubber 59 kg./cm.² against 186 kg./cm.² for 30% aniline resin rubber.) Parallel with this its bound rubber content is very low (Figure 8).

Thus one comes to the conclusion that, for a noticeable reinforcement by resins, chemical bonds between the rubber and the resin particle are desirable. In the case of the condensation resins discussed, the free basic NH₂ group is of great importance for the formation of such chemical bonds. As a confirmation of this hypothesis, one can consider the fact that melamine resin reinforces rubber nearly as well as aniline resin (Figure 2), but that replacement of part of the aniline by *N*-methylaniline, and still more by *N,N*-methylaniline, lowers the modulus, hardness, and abrasion resistance.

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EFFECT OF HEAT TREATMENT ON REINFORCING PROPERTIES OF CARBON BLACK *

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The effect of progressive heat treatment from 1000° to 3000° C on the structure and surface composition of a series of commercial carbon blacks has been described¹. Treatment in this temperature range first removes chemically combined oxygen and hydrogen, and it may safely be assumed that above 1500° C the carbon surface is essentially bare. The area of the carbon blacks, determined by nitrogen adsorption, and the particle size observed under the electron microscope, are not significantly altered by this treatment. However, x-ray diffraction measurements reveal that the size and eventually the ordering of the quasi-graphitic parallel layer groups² composing the carbon black particles increase with increasing temperature¹. The extent of graphitization or internal growth and ordering depends on the particle size of the black. The degree of graphitization increases with particle size. These data are summarized in Table I. Beebe and Young³ have measured heats of adsorption of argon for the series of heat-treated MPC blacks used in this study and report a progressive change toward a more uniform and less active surface with increasing degree of graphitization. Argon adsorption isotherms of the series of heat-treated SFR and FT samples suggest a similar transition⁴.

The present paper reports the change of properties which semireinforcing and fully reinforcing blacks, graphitized to varying degrees, display when compounded in natural rubber.

EXPERIMENTAL

The induction furnace and procedures for heat-treating the carbon blacks have been described¹. The carbon blacks (except the FT grade) were all in the pelleted form. Their properties are reported in Table I.

All stocks were mixed in a Type B Banbury mixer and sheeted on a 6-inch roll mill. In general, 1000-gram batches were prepared. All batches were mixed from a single lot of No. 1 natural rubber (smoked sheet) in the recipe given in Table II. In the case of the slower curing untreated channel blacks, 0.8 part of accelerator was employed. This was decreased to 0.5 part for the furnace- and heat-treated black compounds. The T-50 data indicated that about identical cure rates were attained for all Spheron-6 compounds and comparable Vulcan-3 compounds. Compounds containing coarser particle size Sterling-S and Sterling-FT blacks had consistently lower T-50 values. All stocks were cured at 15, 30, 60, and 90 minutes at 280° F. All stress-strain data reported are for optimum cures. With the exception of the 60-minute cures for the untreated channel blacks, this optimum generally occurred at 30 minutes.

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TABLE I
STRUCTURAL AND ANALYTICAL PROPERTIES OF HEAT-TREATED CARBON BLACKS

Type	Carbon black	Treat- ment temp. ^a (°C)	X-Ray structure			Surface area, (sq. meters/g.) Nitrogen ^b E.M. ^c	Av. particle size (Å)		Volu- tile mat- ter/ (%)	Ash (%)	pH	Electrical resistivity ^d (ohm-cm.)	Den- sity (g./ cc.)
			L_a	L_c	c		d_p^e	d_v^e					
MPC	Spheron-6	—	22.8	13.4	—	114	277	344	5.6	0.07	4.5	17.8	0.46
		1000	36.2	15.5	7.26	91.9				0.03	9.4	0.44	0.30
		1500	44.8	23.3	7.03	88.0				0.05	9.7	0.41	0.36
		2000	75.4	41.9	6.94	85.4				0.00	10.2	0.58	0.39
HAF	Vulcan-3	2700	78.8	48.2	6.90	84.1				0.00	9.0	0.70	0.42
		—	23.5	13.0	—	71.5	235	436	0.7	0.20	9.4	0.56	0.43
		1000	32.5	15.6	7.26	68.1				0.22	8.2	0.44	0.40
		1500	46.5	24.7	7.03	65.4				0.12	9.5	0.39	0.45
SRF	Sterling-S	2000	72.9 ^b	58.3	6.88	62.8				0.03	7.9	0.70	0.47
		2700	76.7 ^b	58.3	6.88	61.9				0.00	7.3	0.77	0.48
		—	25.8	15.2	—	27.9	800	1220	0.4	0.75	9.8	0.58	0.65
		1000	36.2	18.3	7.23	26.0				0.55	10.3	0.25	0.65
FT	Sterling-FT	1500	57.2	36.4	6.95	25.5				0.20	10.6	0.26	0.69
		2000	110 ^b	98.8	25.2	25.2				0.06	10.1	0.51	0.74
		2700	132	121	6.86	24.9				0.00	9.0	0.58	0.74
		—	27.6	16.8	—	15.5	1650	2250	0.4	0.00	8.9	100-110	0.74
		1000	37.5	17.5	7.26	13.1				0.04	8.5	0.24	0.96
		1500	62.0	38.6	6.98	12.9				0.03	9.9	0.19	0.76
		2000	116 ^b	133	6.87	12.6				0.03	7.6	0.34	0.84
		2700	271 ^a	276	6.82	12.5				0.05	6.5	0.38	0.91

^a Time 2 hours.

^b B.E.T. area from nitrogen adsorption at 78° K.

^c Electron microscope surface area values obtained from S.A. = $6 \times 10^3 / 1.86 d_v$.

$$d_v = \frac{\sum_{i=1}^n n_i d_i}{\sum_{i=1}^n n_i} \quad d_p = \frac{\sum_{i=1}^n n_i d_i^2}{\sum_{i=1}^n n_i d_i}$$

^d Weight loss on heating for 7 min. at 950° C in covered platinum crucible.

^e D.E. resistivity of black bed at indicated density under 150 lb./sq. inch compression.

^f Average values from maxima of Smallwood¹ and Studebaker².

TABLE II
COMPOUNDING RECIPE

Ingredients	Parts
No. 1 smoked sheet	100
Carbon black	50
Stearic acid	2.5
Zinc oxide	5.0
Sulfur	2.5
Agerite Hipar	1.0
Santocure	0.5*
	161.5

* 0.8 part Santocure used in batches containing original Spheron-6.

RESULTS AND DISCUSSION

Stress-strain curves for the vulcanizates containing 50 parts of the reinforcing blacks Spheron-6 (MPC) and Vulcan-3 (HAF) and for similar vulcanizates containing the same blacks after heat treatment are reproduced in Figure 1. The most striking effect produced by heat treatment of the carbon black is a drastic reduction of modulus. With the fully reinforcing carbons, this reduction is evident in the 1000° to 1500° C range. Heating these blacks higher, i.e., to 2700° C, produces no further decrease of modulus. In the case of the semireinforcing carbon Sterling-S (SRF), however, a further slight decrease can be obtained by heating the black to 2000° C, as illustrated in Figure 2. With the coarser thermal black, Sterling-FT, there is little change of modulus on heating to 1500° C. The marked change occurs at the 1500° to 2000° level.

With the exception of the HAF black (Vulcan-3), there appears to be no significant loss of tensile strength with heat treatment. This is in line with

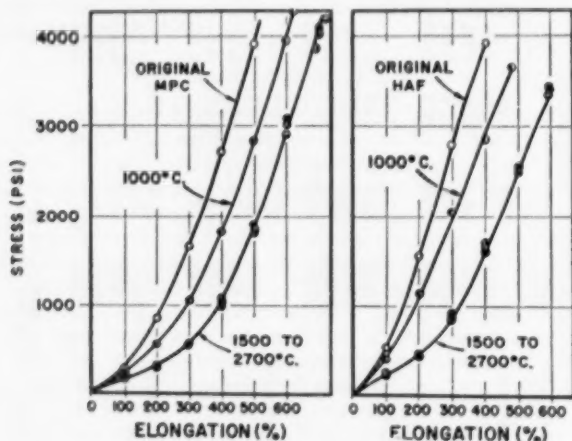


Fig. 1.—Stress-strain curves of rubber compounds containing heat-treated MPC and HAF blacks.

- Original
- ◐ 1000° C.
- 1500° C.
- 2000° C.
- 2700° C.

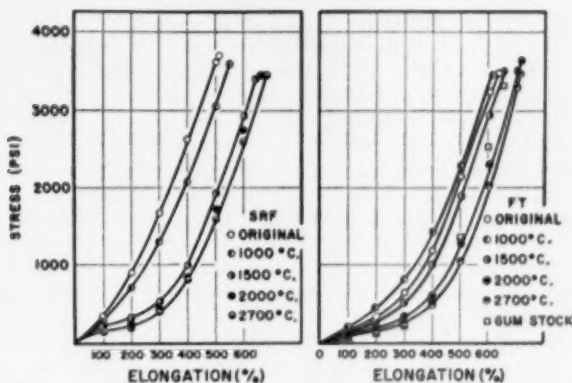


FIG. 2.—Stress-strain curves of rubber compounds containing heat-treated SRF and FT blacks.

generally accepted opinion that tensile strength is primarily a matter of particle size of the black, which is not significantly altered by heat treatment. The loss of tensile strength displayed by the treated HAF black may possibly be associated with some degree of sintering of the particles on heat treatment, although why it should be so pronounced in this case and not with the channel black is not clear.

Turning to the drop of modulus occasioned by heat treatment of carbon black, the question of paramount interest concerns the change of property of the carbon responsible for this decrease. Heating the blacks over the temperature range 1000° to 2700° C has progressively driven the combined oxygen and hydrogen from the surface of the blacks, and, in addition, has induced some internal ordering or graphitization of the blacks. These effects are shown in Figures 4, 5, and 6 of the earlier publication¹. As a measure of the degree of

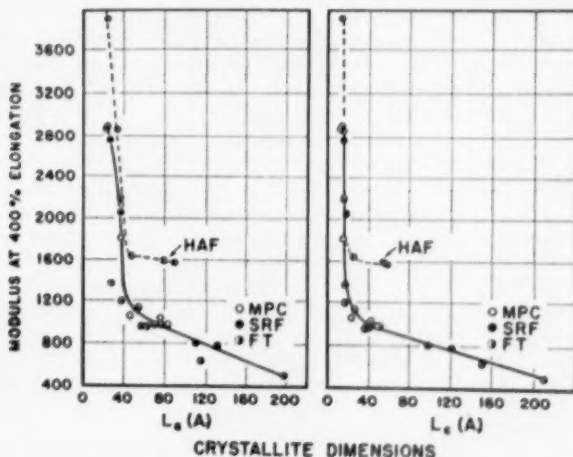


FIG. 3.—Effect of crystallite dimensions on modulus at 400% elongation.

graphitization, the average dimensions, L_c and L_a may be employed. These dimensions, derived from x-ray diffraction measurements, indicate the average thickness or number of platelets per parallel layer group, and the average size of the platelets, respectively. Both increase with increasing treatment temperature, as shown in Table I.

In Figure 3 the modulus at 400 per cent elongation of all stocks studied is plotted against the corresponding L_a and L_c dimensions of the carbons. The striking feature is that the major loss of modulus occurs at low temperatures, where graphitization has not advanced significantly. The slope changes sharply at L_a and L_c values of around 50 and 30 Å, respectively, and, from here on, loss of modulus is not pronounced. From this it may be concluded that the degree of graphitization is not a primary factor in determining the stiffening or modulus properties of carbon black compounds. Referring to Table I, it may be noted that L_a values of 50 Å are attained at 1500° C. At this temperature all carbon blacks are essentially free of combined oxygen and hydrogen¹. Ultimate analyses have confirmed this⁷. Loss of volatile, particularly combined hydrogen, is evidently a prerequisite for graphitization⁸. Accordingly, it must be concluded that the decrease of modulus properties noted on heating to 1000° to 1500° is associated principally with removal of surface hydrogen. The implication is that the outstanding modulus properties which carbon black displays over other filler pigments is due to some type of undefined association between the rubber molecule and a thermally unstable component on the surface of the black.

Smallwood has derived the expression⁵: $M = M_0(1 + 2.5 V)$, to describe the modulus of a system consisting of an elastomer with gum modulus M_0 and containing V volume-per cent of filler. He observed that, with reinforcing carbon blacks, the observed values were much higher than those predicted by this equation. Guth⁹ introduced higher terms and a shape factor to account for the discrepancy. It is interesting to note in Figure 3 that the values of all stocks containing carbon blacks heated to 1500° C and higher are, with the exception of the HAF stock, of the order predicted by Smallwood's expression. The gum stock modulus, M_0 , is about 500 pounds at 400 per cent elongation. All stocks had an equal black loading of 50 parts per 100 of rubber; thus, V is of the order of 20 per cent. Accordingly, the classical stiffening computed from Smallwood's expression is 750 pounds per square inch. With the exception of the HAF stocks, all other blacks heated above 1500° C have 400 per cent moduli, falling in the range 900 to 500 pounds per square inch. In view of the fact that a 50-part black loading and 400 per cent elongation exceed the restrictions of Smallwood's expression, these rough calculations cannot be accepted in any quantitative sense. They are, however, adequate to indicate that the anomalous stiffening effect displayed by the carbon black originally studied by Smallwood is due to an enhanced carbon-to-rubber association. When the source of this association, the chemisorbed hydrogen, is removed by heat treatment, the predicted classical stiffening effect is approached.

The fully reinforcing furnace black (HAF) is unusual in this regard. The modulus properties of this grade of black are not readily destroyed by calcination; as shown in Figure 3, even after heat treatment to 2700° C, they are still capable of producing a 1600-pound modulus at 400 per cent elongation. This modulus cannot be ascribed to volatile matter, and a possible interpretation may involve the fact that HAF blacks possess a greater degree of particle-to-particle association or "structure" than other blacks. This structure is not

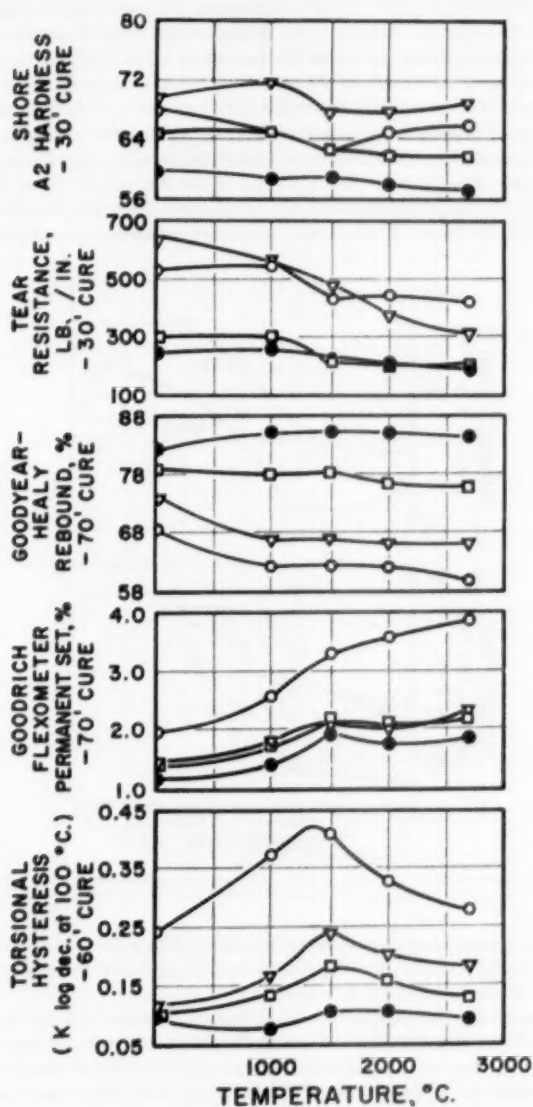


FIG. 4.—Effect of carbon black heat treatment on rubber properties.

- MPC
- ▽ HAF
- SRF
- FT

destroyed by heat treatment. In this instance the high residual modulus may well be accounted for on the basis of a shape factor as suggested by Guth⁹. This interpretation, however, must be accepted with caution, in view of the fact that the resistivity data of Figure 6 show the heat-treated HAF black stocks to be higher in resistivity than the MPC stocks. If the former possessed a higher degree of structure, a lower resistivity might be anticipated.

Standard laboratory test data were collected on all vulcanizates¹⁰. In general, the results were much less striking than those observed for modulus properties. Shore hardness showed no significant change with increasing heat treatment of the blacks. Tear resistance and resilience properties decreased

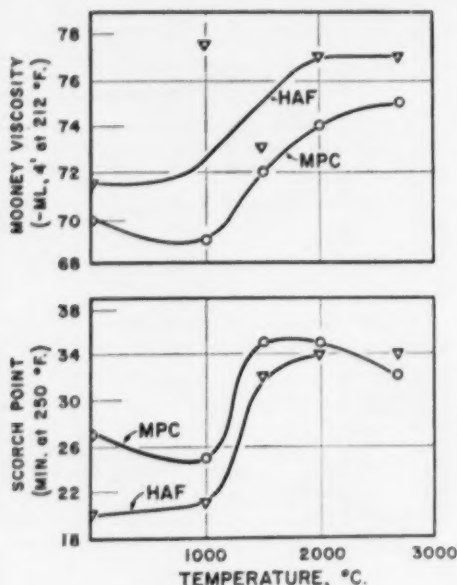


Fig. 5.—Mooney viscosity and scorch point of rubber compounds containing heat-treated MPC and HAF blacks.

slightly, while permanent set showed a slight increase. Torsional hysteresis went through a slight maximum for stocks loaded with blacks treated at 1500°C. These results are summarized in Figure 4.

Mooney viscosity data reproduced in Figure 5 show only a slight increase. An unexpected result was obtained when the Mooney scorch time of the stocks containing the heat-treated blacks was measured. These data are also presented in Figure 5. The "scorch" properties, or premature vulcanization, which furnace blacks display in rubber stocks are usually associated with their low volatile content. Thus, as may be observed in Figure 5, the unheated HAF black with a volatile content of only 1 per cent had a scorch time of 20 minutes, while the MPC black with a volatile content of 5 per cent had a scorch time of 27 minutes. The scorch time of a furnace black can be improved by increasing its volatile content by air aftertreatment¹¹. By the same token, it would be anticipated that removal of volatile matter from a black should decrease the

time required to scorch. Surprisingly enough, the authors' data indicate quite the reverse; when both the chemisorbed oxygen and hydrogen are completely removed by heating to 1500° C, the time required to scorch actually increases. The data shown in Figure 5 are for only the HAF and EPC stocks; however, similar results were found for the other blacks. Tentatively, the results can be explained by assuming that the combined hydrogen on the surface of the black accelerates vulcanization and that effect of combined oxygen is one of removing or neutralizing active surface hydrogen. When any black is heated to 2000° C, an essentially bare carbon surface is obtained, and the scorch and cure time of all blacks should be essentially the same. Data in Figure 5 indicate this to be the case.

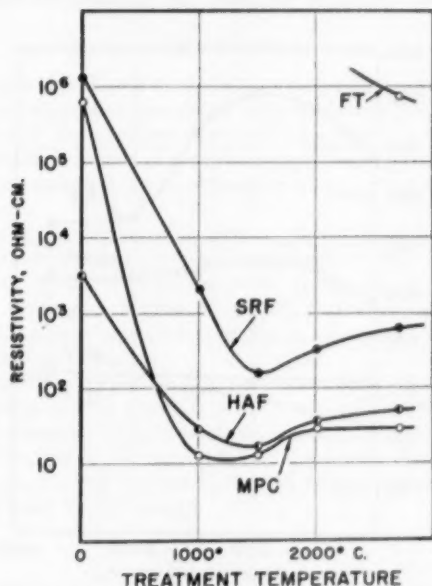


Fig. 6.—Direct current resistivity of rubber compounds containing heat-treated carbon blacks.

In an earlier publication¹ describing the preparation and properties of heat-treated carbon blacks, the direct current resistivity of all heat-treated carbon blacks passed through a minimum at 1500° C. The major decrease of resistance coincided with cleaning all chemisorbed oxygen and hydrogen from the surface, i.e., heating at 1000° to 1500° C. The increase of resistivity noted on heating to 1500° to 2000° was associated with internal crystallite growth and a decrease of the number of contacts within the particle. In these measurements, made on the dry black, the coarsest blacks developed the lowest resistivity on heat treatment. In the present work, the resistivity of natural rubber vulcanizates containing 50 parts of these same blacks has been measured. The results are presented in Figure 6. Here the observations with regard to conductance and particle size are reversed. The coarsest black, which in the dry state showed the minimum resistance, produces vulcanizates of the highest resistance. This result, of course, is not unexpected. It does, however,

emphasize the fact that, in a carbon-loaded vulcanizate, the number of carbon-to-carbon contacts, or conducting paths, is of primary significance. Presumably if it were possible to load a rubber stock high enough to approach closest packing of carbon particles, the effect of particle size would disappear, and the conductance of the carbon itself would determine resistivity.

The question of paramount interest is the effect of heat treatment of carbon black on its ability to impart abrasion resistance to rubber. In view of the drastic reduction of modulus which seems to follow the removal of surface chemisorbed hydrogen, one might anticipate an equally drastic reduction of resistance to abrasive wear if modulus does indeed play a dominant role in rubber reinforcement. Since the heat treatment of these blacks was carried out in a laboratory induction furnace, the quantity of black available for

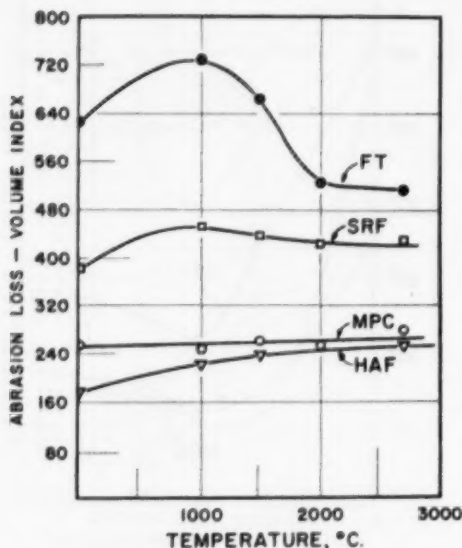


FIG. 7.—Abrasion loss of rubber compounds containing heat-treated carbon blacks.

abrasion testing was necessarily limited. Consequently, most of the study was confined to laboratory evaluation on the Akron angle abrader. Some of the results are presented in Figure 7. Neither the FT nor SRF grades of carbon black showed any very significant change of abrasion properties on heat treatment. This was not unexpected, since these blacks are not considered to be fully reinforcing. However, the laboratory data on the fully reinforcing MPC and HAF grades were somewhat unexpected. The MPC black did not show significant change of abrasion loss on heat treatment. The maximum spread in hardness of the MPC stocks was only one Shore point, and, in the case of the HAF stocks, the spread was but two points. However, results obtained on a laboratory angle abrader often bear little relation to the results obtained in actual tire performance. The Lambourn abrader is held in much higher regard¹². Samples of MPC and MPC heated to 2700° C were evaluated by Parkinson, who reports a wear rating of 70 per cent for the vulcanizates con-

taining the 2700° sample, based on 100 per cent for the original MPC. Juve¹² reports a wear rating of 71 per cent for the heat-treated black based on 100 per cent for the original MPC. Electron-microscope examination of these treads showed about equivalent dispersion of the blacks. The 70 per cent ratings must, of course, be accepted over the laboratory abrasion data presented in Figure 7.

While the present data, particularly with regard to abrasion resistance, are inadequate, they demonstrate that the chemical nature of the carbon black surface is the major factor in determining modulus, curing properties, and electrical conductivity of carbon-reinforced vulcanizates. On the other hand, when one considers reinforcement in terms of resistance to abrasive wear, it appears that the major factor is particle size of the carbon black.

SUMMARY

The high degree of stiffness or modulus which reinforcing carbon blacks impart to rubber has often been associated with reinforcement. Modulus appears to be associated with the chemical nature of the carbon black surface; when the carbon black surface is cleaned of combined oxygen and hydrogen, a drastic drop in modulus occurs, and this is not accompanied by an equally drastic decrease in tire road wear.

Reinforcing and semireinforcing carbon blacks have been heat-treated at successive increments through a temperature range of 1000° to 2700° C. Treatment up to 1500° results in removal of all combined oxygen and hydrogen, followed by an increasing degree of graphitization at higher temperatures. These carbon blacks have been compounded in a standard natural-rubber compound and properties evaluated.

Modulus is profoundly altered by the chemistry of the carbon surface. Electrical resistivity passes through a minimum at 1500° C. Scorchiness or premature vulcanization improves with removal of volatile matter. The degree of graphitization of the carbon has only a minor effect on rubber properties. A highly graphitized carbon black still imparts a high degree of resistance to abrasive wear to tire treads.

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- ¹² The authors are indebted to Donald Parkinson for providing data from the Dunlop Rubber Company laboratory.
- ¹³ A. E. Juve, B. F. Goodrich Research Center, Breckville, Ohio, kindly consented to build and road-test a natural-rubber tread loaded with 50 parts of the 2700° heat-treated MPC black.

GEL STRUCTURE. VI. PREPARATION OF GELS AND GLOBULAR STRUCTURES FROM RUBBERS BY VULCANIZATION OF SOLUTIONS *

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The present article describes experimental results obtained in a study of the properties of gels and globular structures formed from natural rubber (smoked sheet) and synthetic rubber (polybutadiene). These experiments were inspired primarily by the necessity of developing a method of judging the structure of the molecules of various elastomers. The solution of this problem is of great practical importance, since many properties of elastomers are determined by the nature of the structure of their molecules.

In our studies of the mechanism of formation of protein gels¹, it was shown that gels have various relaxation properties during deformation, depending on the concentration. Larger mechanical losses take place in concentrated gels than in dilute gels. However, it can be assumed that the relaxation processes depend, not only on the concentration, but also on the molecular structure of the gel-forming substance. In particular, gels prepared from polymers containing side chains must have a wider range of relaxation periods than those prepared from linear polymers.

Rubber gels were prepared by vulcanization of 20 per cent toluene solutions of rubber with sulfur monochloride (3 per cent of weight of the rubber) at room temperature. Before being dissolved, the rubbers were masticated about 5 minutes on a cold mill. The toluene was first dried on calcium chloride and distilled; the sulfur monochloride was saturated with sulfur and distilled over the excess sulfur. A 4 per cent solution of sulfur monochloride in toluene was used to prepare the gels.

After the sulfur monochloride solution was added to the rubber solution, the mixture was carefully stirred and poured into aluminum beakers in which the mechanical tests of the gels formed were then made. This was usually done the next day after their preparation. In order to prevent evaporation, the beakers containing the gels were kept in a pan of glycerol, with a glass cover, until they were tested. For the same reason, glycerol was added to the beakers of gels during measurement of deformation at temperatures above 25° C.

The mechanical properties of the rubber gels, like those of gelatin gels studied earlier¹, were measured with an Aleksandrov-Gaev frequency apparatus.

Figures 1 and 2 show data on the temperature relation of the deformation of gels of natural and synthetic rubbers. It is seen from the figures that the deformation of a gel of natural rubber begins to develop at about -50° C; at higher temperatures, a rapid increase of the deformation independent of the rate of the deforming force is observed; at -30° C, the deformation reaches a maximum value, which remains almost constant to 100° C.

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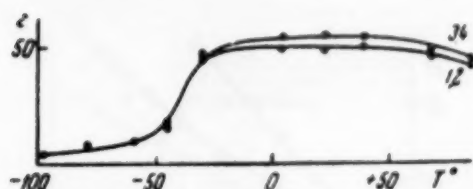


Fig. 1.—Deformation of gels of natural rubber: measured at four frequencies (oscillations per minute): (1) 1000, (2) 100, (3) 10, (4) 1. The ordinate indicates ϵ , the abscissa the temperature.

The absence of elasticity in gels of natural rubber at temperatures below -50°C was evidently caused by crystallization of the rubber. The abrupt rise of the deformation-temperature curve at about -50°C is due to fusion of the rubber and conversion of the system into the high-elastic state. Consequently, gels of natural rubber behave just like dilute gelatin gels treated with quinone, that is, throughout the temperature range the frequency relation is practically absent.

A different picture is observed in the deformation of a gel prepared from a solution of polybutadiene rubber (SK-B). The appearance of deformation in this gel begins at about -100°C . The deformation has a pronounced relaxation character. When the temperature increases, the relation of the magnitude of the deformation to the rate of deformation at first increases and then falls. At a temperature of about 50°C , large relaxation periods disappear almost completely. This type of deformation of gel is evidently related to side-chain formation in the macromolecules of the polybutadiene rubber. Thus, on the basis of the study of the mechanical properties of gels, it is possible to determine differences in the formation of the chain molecules of natural and synthetic rubbers. Side-chain formation in the polymer molecules must be reflected not solely in the nature of the intermolecular reaction. This characteristic structure of the macromolecules naturally must also appear in intramolecular reactions, that is, in the formation of globular structures. The linear side-chain structure of the molecules must be reflected in the specific volume and shape of the globules formed.

In order to verify these assumptions, we set up experiments on the preparation of globular structures from natural and synthetic rubbers. The degree of globulization was determined by measuring the viscosity of rubber solutions during vulcanization.

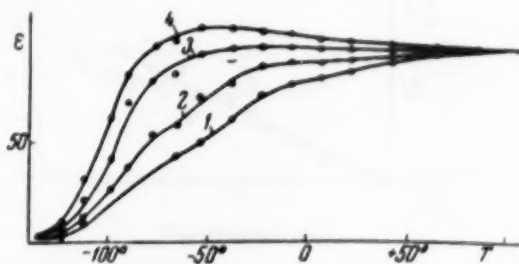


Fig. 2.—Deformation of gels of synthetic rubber: measured at four frequencies (oscillations per minute): (1) 1000, (2) 100, (3) 10, (4) 1. The ordinate indicates ϵ ; the abscissa the temperature.



FIG. 3.—Relation of concentration to the viscosity of solutions of globular slightly milled rubbers: (1) Natural rubber + 500 per cent S_2Cl_2 ; (2) Natural rubber + 50 per cent S_2Cl_2 ; (3) Synthetic rubber (SKR) + 500 per cent S_2Cl_2 . The ordinate indicates the specific viscosity η_{sp} ; the abscissa the % concentration.

In distinction from albumins², the intermolecular reaction leading to the formation of globular structures in the case of rubbers was effected by vulcanization of 0.16 per cent toluene solutions of natural and synthetic rubbers at 95° C with sulfur monochloride. The toluene and sulfur monochloride were purified, just as in the study of gels. Both the kinetics of formation of globular structures and the relation of the concentration to the viscosity of solutions of globular rubbers were studied.

The influence of the proportion of sulfur monochloride and the molecular weight of the natural rubber on globulization were also investigated. Natural rubbers of various molecular weights were obtained by varying the time of mastication. In order to determine the relation between concentration and viscosity, solutions of globular rubbers were concentrated in a vacuum at 40–45° C, and their viscosities as a function of the dilution were measured.

As is seen from Figures 3 and 4, solutions of natural rubber, regardless of the molecular weight of the original rubber and the proportion of sulfur monochloride, maintain a linear relation between concentration and viscosity up to a concentration of approximately 1 per cent, and solutions of polybutadiene rubber up to 0.4 per cent. The data obtained can be explained by the fact that the globules formed from the flexible, linear natural-rubber molecules are more similar to spherical particles than the synthetic-rubber globules.



FIG. 4.—Relation of concentration to the viscosity of globular rubbers: (1) Natural rubber slightly milled + 500 per cent S_2Cl_2 ; (2) Natural rubber highly milled + 500 % S_2Cl_2 . The ordinate indicates the specific viscosity η_{sp} ; the abscissa the % concentration.

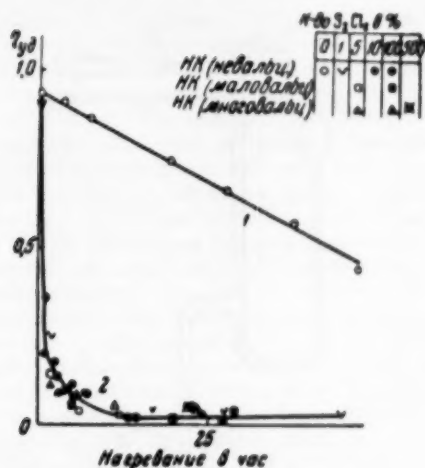


Fig. 5.—Kinetics of globulization of solutions of natural rubber in the presence of 1 to 500% S_2Cl_2 (2), and change of the viscosity of solutions in the absence of S_2Cl_2 (1). The ordinate indicates the specific viscosity η_{sp} ; the abscissa the time of heating in hours.

The kinetics of formation of globular systems was studied by the following method. After the viscosity of the original solution was measured, a 20 per cent toluene solution of sulfur monochloride was added to it and the mixture was carefully stirred; then the viscosity of the mixture was measured. Following this, the solution was heated to 95° C, and its viscosity was measured at intervals. The solution was heated until a definite viscosity was established.

The data in Figures 5 and 6 show that the addition of sulfur monochloride to solutions of natural rubber causes a sharp drop of viscosity; the limiting value of the viscosity does not depend on the molecular weight of the rubber, nor on the proportion of sulfur monochloride. This indicates that the globules formed from natural rubber have a constant specific volume. A higher viscosity is obtained under similar conditions with solutions of synthetic rubber; this is evidently due to the more fragile packing of the globules.

In the case of synthetic rubber, the maximum value of the viscosity is established after a longer period. It is seen from Figure 5 that, during heating



Fig. 6.—Kinetics of globulization of solutions of natural rubber in the presence of S_2Cl_2 : (2) 1%, (3) 10%, (4) 100%, and change of viscosity of solution in the absence of S_2Cl_2 (1). The ordinate indicates the specific viscosity η_{sp} ; the abscissa the time of heating in hours.

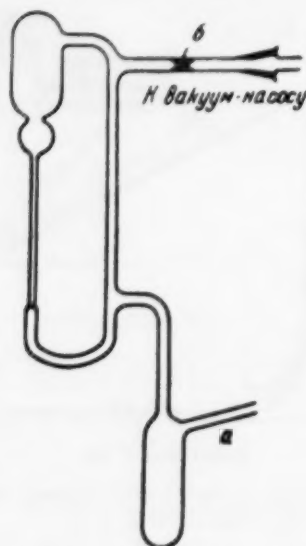


FIG. 7.—Diagram of the vacuum viscometer. The side-tube (sealed at *b*) leads to the vacuum pump.

of solutions of natural rubber which contain no sulfur monochloride, a certain decrease of viscosity is also observed. In this case, the decrease of viscosity is caused by the destruction of the natural-rubber molecules as a result of their reaction with atmospheric oxygen.

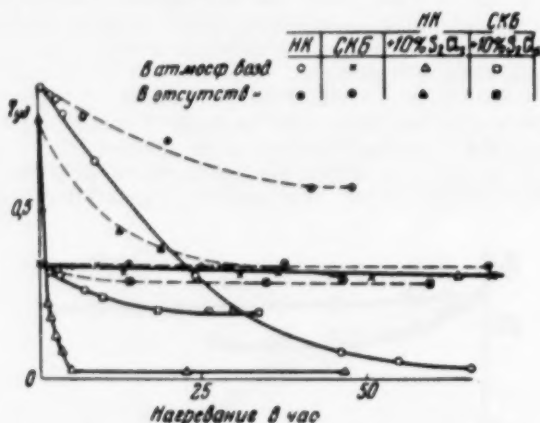


FIG. 8.—Kinetics of globulization of rubber solutions. The ordinate indicates the specific viscosity η_{sp} ; the abscissa the time of heating in hours. The block data on the diagram are as follows:

	Natural rubber	SK-B rubber	Natural rubber 0% S ₂ Cl ₂	SK-B rubber 10% S ₂ Cl ₂
In air	○	×	△	□
Exclusion of air	●	●	▲	■

In order to exclude the influence of oxygen, we made experiments in the absence of air. Viscometers which make it possible to study the kinetics of the formation of globular rubbers in the complete absence of air were constructed for this purpose. A diagram of a vacuum viscometer is shown in Figure 7.

The method of working with vacuum viscometers was as follows. The rubber solution and the sulfur monochloride solution (10 per cent S_2Cl_2 by weight of rubber) were poured into the ampoule of the viscometer through the side-tube *a*. After the side-tube was sealed, the air was eliminated with a high-vacuum apparatus by repeated freezing and thawing of the solution with liquid nitrogen. Then the viscometer was removed from the vacuum apparatus by resoldering the connecting tube *b* and was transferred to a thermostat for the measurement of the viscosity. The first measurement of viscosity was made before heating and the following measurements after heating at 95° C.

Figure 8 shows data for the change of viscosity of natural-rubber and polybutadiene synthetic-rubber solutions, with and without added sulfur monochloride, as a function of the time of heating at 95° C in the presence and in the absence of air. It is seen from these data that sulfur monochloride causes a decrease in the viscosity of natural-rubber solutions, both in the presence or absence of air. The greater decrease of viscosity of solutions of natural rubber in the presence of air and sulfur monochloride is evidently due, not only to globulization, but also to destruction of the molecules of natural rubber caused by atmospheric oxygen.

In polybutadiene rubber solutions, the decrease of viscosity during vulcanization in air is very small, and is not observed at all after the elimination of air. On the basis of these data, one can conclude that the intramolecular reactions (globulization of the molecules) do not take place in solutions of synthetic rubbers.

CONCLUSIONS

1. The mechanical properties of gels prepared from solutions of natural rubber and synthetic rubber were studied.
2. It was established that gels of synthetic rubber (polybutadiene rubber) have a wide range of relaxation periods. Gels of natural rubber (smoked sheet) behave like ideally elastic substances, following Hooke's law in the change of rate of deformation by 1000 times.
3. The viscosity of solutions of natural rubber and of polybutadiene rubber in the presence of sulfur monochloride was studied.
4. We observed that sulfur monochloride sharply decreases the viscosity of natural rubber solutions and has almost no influence on the viscosity of synthetic rubber solutions.

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CHLORINATION OF RUBBER AND SOME PRODUCTS OF ITS PARTIAL CHLORINATION *

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By the prolonged action of chlorine, rubber is converted into a hard white product which is quite inelastic and is characterized by its remarkable stability toward heat and chemical reagents. At the present time this product, which analyzes 65.5 per cent chlorine and conforms to the empirical composition¹, $(C_{10}H_{11}Cl_7)_n$, is believed to have, not the straight-chain structure of rubber itself, but a cyclic structure².

Although numerous investigations have been carried out to throw light on the mechanism of chlorination, the mechanism is still not well understood, particularly with respect to any cyclization reactions which may occur. The present author has taken up the study of the chlorination of rubber and of partially chlorinated products by both physical and chemical methods, including fractionation, chlorine analyses, viscometry, osmometry, infrared analysis, and the reactivity of the chlorinated rubber products to aniline³.

PREPARATION OF PARTIALLY CHLORINATED PRODUCTS. PURIFICATION AND FRACTIONATION

A series of samples of partially chlorinated rubbers were prepared by the controlled action of chlorine (diluted with nitrogen twenty-fold by volume) on 1.5 per cent solutions of rubber in carbon tetrachloride³. These operations covered a period of two hours at about 25° C. The approximate quantity of chlorine reacting to obtain a product of given chlorine content was calculated from the reactions proposed by Bloomfield¹:



After precipitation by alcohol and solution in toluene, the products were fractionated by successive additions of methanol or ethanol. Because of their poor stability, the partially chlorinated rubber products, which are preserved in solution in carbon disulfide, should be studied promptly.

DEGREE OF HOMOGENEITY OF THE PARTIALLY CHLORINATED RUBBER PRODUCTS

The chlorine contents of the various fractions of partially chlorinated rubbers were determined by semimicroanalysis according to the method of Parr⁴ (see Table 1).

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*. Vol. 32, No. 3, pages 229-236, March 1955.

TABLE I

Sample	Fraction	Weight (in grams)	Chlorine content (%)
I		8.93	9.2 (mean)
	F 1	1.13	31
	F 2	2.63	5.3
	F 3	2.95	7
	F 4	2.22	6
II		10.41	17.4 (mean)
	F 1	3.38	33
	F 2	4.05	9
	F 3	1.95	12
	F 4	1.03	8.5
III		18	26 (mean)
	F 1	11	33
	F 2	3	18
	F 3	4	13.5
IV		16.67	28.3 (mean)
	F 1	12	32
	F 2	2.75	21.5
	F 3	1.92	14
V		19.02	36
	F 1	3.17	36
	F 2	5.30	36.2
	F 3	4.90	36.1
	F 4	2.65	36.1
	F 5	3	34
VI		18.41	39
	F 1	3.76	38.5
	F 2	3.27	39
	F 3	7.34	39
	F 4	4.04	38
VII		18.32	44
	F 1	6.48	44.5
	F 2	2.90	44.3
	F 3	4.63	44.5
	F 4	4.31	43

The first four samples were highly heterogeneous in chemical composition, but all contained an initial fraction showing by analysis 31–33 per cent chlorine, in contrast to products which are often much less chlorinated. Furthermore, the initial fraction of each of the samples represented 12.6, 32.4, 61, and 72 per cent, respectively, by weight of the total product of samples I–IV, containing 9.2, 17.4, 26, and 28.3 per cent, respectively, total chlorine. By extrapolation of these results as a function of the mean chlorine content of the corresponding partially chlorinated rubbers, it was found that, around 34–35 per cent chlorine, the initial fraction represented the total chlorine content of the sample. In other words, a sample containing 34–35 per cent chlorine should be of practi-

cally uniform composition. However, the chlorine contents of the initial fractions would indicate homogeneity around 31-33 per cent chlorine. This anomaly is only apparent. Actually, a new fractionation of these initial fractions (see Table 2) showed that they all contained 34-35 per cent chlorine and their slightly lower mean chlorine contents are attributable to less highly chlorinated molecules entrained in the precipitation of the initial fraction.

The homogeneity of rubbers containing more than 35 per cent chlorine is, in fact, verified by a study of samples V, VI, and VII (see Table 1), which had mean chlorine contents of practically 36, 39, and 44 per cent. The different fractions obtained from the same sample had practically identical chlorine contents, except for the final fraction, which analysis showed to have a slightly lower chlorine content. An explanation of this phenomenon will be offered later. The homogeneity of highly chlorinated rubber has been established by Alliot⁵.

In summary then, rubbers with relatively low chlorine contents which have been prepared by the direct action of chlorine on crepe rubber in solution are very heterogeneous, as has already been shown by van Amerongen and collaborators⁶. However, all these products contain components with 34-35 per cent chlorine.

TABLE 2

Sample II F 1	{ F 1'	0.7 g. 34.2% Cl
	{ F 2'	2.4 g.
Sample III F 1	{ F 1'	4 g. 34.5% Cl
	{ F 2'	33 % Cl
	{ F 3'	29 % Cl
Sample IV F 1	{ F 1'	7 g. 34 % Cl { F 1'' 1 g. 34.8% Cl
	{ F 2'	5 g. 29.5% Cl { F 2''

Rubbers analyzing higher than 35 per cent chlorine are, on the contrary, practically homogeneous.

It should be noted that this chlorine content, 35 per cent, which marks a sharp change in the rate of chlorination, corresponds in substance to the end of the first stage in the reaction mechanism proposed by Bloomfield¹:



MOLECULAR DIMENSIONS OF PARTIALLY CHLORINATED RUBBERS

CHANGE OF VISCOSITY DURING CHLORINATION

We have studied the changes of the relative viscosity of solutions of rubber undergoing chlorination³ (see Figure 1). It was found that, from the beginning of chlorination, the viscosity decreased progressively to a chlorine content around 35 per cent; after a period of constancy in this range, the viscosity tended to increase. This fairly regular decrease of viscosity at the beginning is the result, for the most part, of a change in the structure of the macromolecules, involving a notable shortening of these molecules.

RELATIONS BETWEEN VISCOSITY AND MOLECULAR WEIGHT

The intrinsic viscosity $[\eta]$ and the molecular weight M of a high polymer are related by the general law proposed by Kuhn⁷: $[\eta] = K.M^\alpha$, where K and

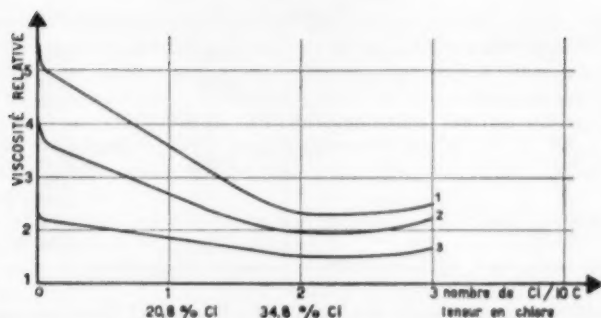


FIG. 1.—Viscosity of three solutions of chlorinated rubber as a function of their degree of chlorination. Solution 1—Concentration 1% by weight. Solution 2—Concentration 0.5% by weight. Solution 3—Concentration 0.5% by weight (rubber more highly degraded than that in Solution 2). The upper scale of the abscissa indicates the number of chlorine atoms per 10 carbon atoms; the lower scale the percentage chlorine content. The ordinate indicates the relative viscosity.

α are constants characteristic of a polymer with respect to a given solvent. As far as the chlorination of rubber is concerned, the change which the coefficient K shows as a function of the chlorine content can furnish useful information on the progressive changes in the formation of this product.

In addition, the intrinsic viscosities $[\eta]$ and the molecular weights M of different fractions of partially chlorinated rubber were determined (see Table 3). These measurements were made with toluene solutions at 25° C by means

TABLE 3

Chlorine content (%)	$[\eta]$ 1	M 2	$[\eta']$ 3	M' 4
0	6.7	450,000	6.7	450,000
	6.4	420,000	6.4	420,000
	4.4	237,000	4.4	237,000
	2.75	132,000	2.75	132,000
	1.05	34,000	1.05	24,000
11.5	0.53	18,300	0.595	16,400
27.5	0.60	54,000	0.82	39,600
29	0.42	43,200	0.60	30,000
33	0.90	54,000	1.32	37,000
35	2.04	445,000	3.06	296,000
	1.1	196,000	1.66	130,000
39	3.04	945,000	4.90	587,000
	2.63	746,000	4.24	463,000
	1.66	405,000	2.68	251,000
47	1.05	293,000	1.95	158,000
	0.92	240,000	1.70	130,000
59	1.36	734,000	3.24	310,000
	1.03	490,000	2.45	206,000
	0.79	345,000	1.88	145,000
	0.55	214,000	1.32	90,000

TABLE 4

Chlorine content (%)	α	$10^4 K$	$10^4 K'$
0	0.717	5.98	5.98
11.5	—	—	5.28
27.5	—	—	4.16
29	—	—	3.69
35	—	1.80	3.59
39	—	—	3.59
47	—	—	3.69
59	—	—	3.77
65.5*	—	0.6	3.51

* The results for completely chlorinated rubbers have been taken from Alliro².

of an Oswald viscometer on the one hand and a Fuoss and Mead osmometer³ on the other hand³.

The K values and α values of the different chlorinated rubbers are recorded in Table 4 (columns 1 and 2). The coefficient α remains the same from the original natural rubber to the completely chlorinated rubber. On the contrary, the K coefficient changes most significantly. However, these changes are the result, not only of changes of structure which take place during chlorination, but also of the increase of the weight of the C_{10} groups of the macromolecule by fixation of chlorine. This results, in effect, both in a higher molecular weight and, independent of any change of structure, in a decrease of the intrinsic viscosity in the relation where the concentration is expressed in the denominator. As a result of the influence of changes in the weight of the elemental linkage on the K value, the relation: $[\eta] = K.M.\alpha$, as it has been defined, is less useful in following the progressive change of structure of rubber in the course of its chlorination.

In addition, we have derived a viscosity-molecular weight relation in which these changes of weight are not a factor. In this relation: $[\eta'] = K'.M'.$, α ,

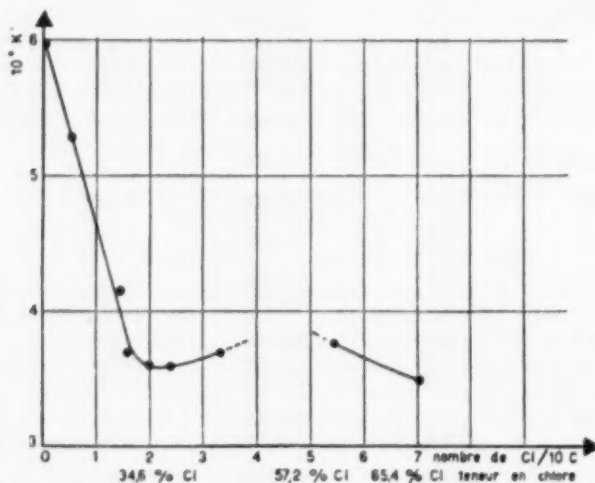


Fig. 2.—Values of the K' coefficient as a function of the degree of chlorination. The upper scale of the abscissa indicates the number of chlorine atoms per 10 carbon atoms; the lower scale the percentage chlorine content.

$[\eta']$ and M' represent the viscosity and the molecular weight, respectively, reduced to terms of natural rubber; i.e., M' is not the true molecular weight M of a chlorinated rubber but is that of a natural rubber containing the same number of carbon atoms. In the same way, in calculating the intrinsic viscosity $[\eta']$, we have used, not the true concentration, but the corresponding concentration of natural rubber. In this new relation, $[\eta'] = K' M' \alpha$, changes of K' are attributable solely to changes in the structure of the rubber during its chlorination.

The $[\eta']$ values and M' values are recorded in Table 3 (columns 3 and 4) and the K' values in Table 4 (column 3).

The results are in accord with those of Staudinger⁸. In reality, the decrease of the coefficient K' (Figure 2) is further evidence of a considerable shortening of the macromolecular chains, independent of any degradation reactions, as a result of chlorination. This transformation should be complete at a chlorine content of 35 per cent. Above this point, the molecular dimensions do not seem to change further to any significant extent.

It should be noted, however, that we have not been able to obtain reproducible measurements of the viscosities and molecular weights of rubber analyzing between 50 and 57 per cent chlorine. It would seem that these measurements are rendered invalid in this range of chlorine contents by physical phenomena of molecular association.

INFRARED STUDY OF PARTIALLY CHLORINATED RUBBERS

The spectra of a series of fractions of natural rubber and partially chlorinated rubbers were determined. The measurements were made with films by means of a Beckman spectrophotometer⁹ Model IR-2. It is difficult to prepare films of strictly constant thickness. However, an observation made by Alliot and Orsini¹⁰, and by the present author has shown that the spectral line 6.9μ does not change to any appreciable degree from natural rubber through to completely chlorinated rubber. Furthermore, by making use of the law of Beer and Lambert, it is possible to transform the spectra of films in such a way as in all cases to reduce the intensity of the 6.9μ spectral line to the same value. The spectra thus transformed correspond to the same molecular concentration, and consequently can be studied on a comparative basis.

The intensities of the principal spectral lines of the various samples studied and of highly chlorinated rubbers¹⁰ are recorded in the log (I_0/I) form in Table 5. Here I/I_0 represents the transmission ratio.

Rubbers in a low state of chlorination show spectra almost identical to the spectrum of natural rubber. With progressive increase of the chlorine content, the differences become greater until, for products containing 35 per cent chlorine, the spectra are distinctly different from the spectrum of rubber itself, and show many similarities with the spectrum of completely chlorinated rubber (see Figure 3). It will be observed that the spectral line 12μ , attributed by Richardson and Sacher¹² to the configuration: $\text{RC}(\text{CH}_2):\text{CHR-cis}$, has disappeared. On the other hand, the spectral line 6μ , attributable to a $-\text{C}=\text{C}-$ vibration remains constant to a point approaching 35 per cent chlorine, then increases abruptly at this point, then decreases uniformly until, around 55 per cent chlorine, it becomes inappreciable.

The disappearance of the 12μ spectral line is an indication of a structural change, which is probably the result of cyclization reactions. This hypothesis is confirmed by the appearance and increase of the 8μ and 11μ spectral lines,

TABLE 5

Chlorine content (%)	log (I ₀ /I)					
	Line 3.4 μ	Line 6 μ	Line 6.9 μ	Line 8 μ	Line 11 μ	Line 12 μ
0	0.520	0.106	0.556	0.124	0.054	0.538
7	0.493	0.119	—	0.180	0.213	0.528
12	0.560	0.120	—	0.202	0.375	0.372
14	0.435	0.108	—	0.204	0.426	0.386
21.5	0.393	0.108	—	0.194	0.560	0.352
29.5	0.375	0.158	—	0.350	0.812	0.326
33	0.312	0.164	—	0.380	1.115	0.312
34	0.349	0.254	—	0.364	0.988	0.307
35	0.361	0.335	—	0.384	0.982	0.300
39	0.338	0.252	—	0.497	0.940	—
43	0.271	0.183	—	0.496	0.910	—
44.5	0.257	0.197	—	0.450	0.908	—
54.5	0.196	—	—	0.680	0.706	—
59.	0.161	—	—	0.780	0.596	—
63	0.127	—	—	0.875	0.500	—
65.5	0.120	—	—	0.950	0.550	—

which give to chlorinated rubber containing 35 per cent chlorine a spectrum closely analogous to that of cyclohexane (see Figure 3). All the important spectral lines, i.e., 3, 4, 6.9, 8, 9.7, and 11 μ , are common to each, the 6 μ line being the only exception. This latter has, as already mentioned, been attributed to double bonds, and consequently is absent in the spectrum of cyclohexane but is present in that of cyclohexene.

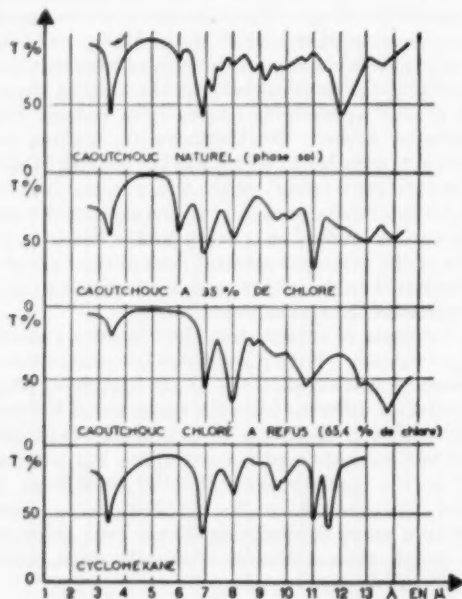


FIG. 3.—Infrared transmission spectra. The abscissa indicates the wave length λ in μ units. The top graph is the sol phase of natural rubber, that below is chlorinated rubber containing 35% chlorine, that next below is completely chlorinated rubber (65.4% chlorine), and the lowest graph is cyclohexane.

Above a chlorine content of 35 per cent, the 8μ spectral line continues to increase to the point of complete chlorination. The 11μ line, on the contrary, after a maximum at 35 per cent chlorine, decreases to a point around 60 per cent chlorine until it becomes virtually constant above this percentage. As for the 3.4 and 6.9μ spectral lines, both of which are attributable to C—H vibrations¹², the first becomes slowly weaker from natural rubber to completely chlorinated rubber, whereas the second maintains practically the same intensity.

In summary, then, the infrared study of partially chlorinated rubbers gives evidence of structural changes before a chlorine content of 35 per cent is reached, as indicated by the progressive disappearance of the 12μ spectral line, the appearance of the 11μ line, etc., and around the 35 per cent point, as indicated by the sudden increase of the 6μ line. These changes seem to be the result of cyclization reactions, which involve the formation of C_6 rings, analogous to the spectrum of cyclohexane.

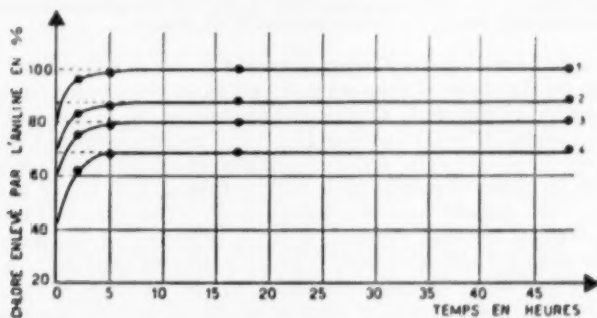


Fig. 4.—Percentage of chlorine removed by aniline as a function of the time at 100°C : 1. Rubber containing 27% chlorine. 2. Rubber containing 34% chlorine. 3. Rubber containing 35% chlorine. 4. Rubber containing 35.5% chlorine. The abscissa indicates the time in hours; the ordinate the percentage chlorine removed by aniline.

Above 35 per cent chlorine content, there are no further changes in the structure. The changes in the spectrum, which are rather small, are apparently the result of simple fixation of chlorine, which leads to the final disappearance of the last double bonds around 55 per cent chlorine.

It should be noted that our results on the changes of the spectral lines are in satisfactory accord with those of Salomon, van der Schee, Ketelaar, and van Eyk¹³, although these authors attribute the weakening of the 12μ spectral line and the simultaneous increase of the 11μ line to a displacement of the double bonds, which would become of the vinyl type. Double bonds of this type should still be present in highly chlorinated rubbers.

REACTIVITY OF CHLORINATED RUBBERS TOWARD ANILINE

According to their position in the molecule, the chlorine atoms react more or less rapidly with organic bases. This reaction can be taken advantage of for the identification of halogenated groups in polymers¹⁴. Thus, van Amerongen, Koningsberger, and Salomon⁶, as a result of a study of the reaction of chlorinated rubbers with aniline at 100°C , came to the conclusion that chlorine at first combines with rubber chiefly by substitution in the allylic position, and that displacements of double bonds take place during progressive chlorination.

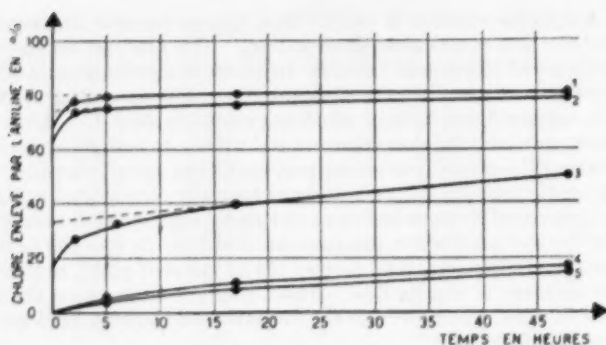


FIG. 5.—Percentage of chlorine removed by aniline as a function of the time at 100° C. 1. Rubber containing 39% chlorine. 2. Rubber containing 44.5% chlorine. 3. Rubber containing 55% chlorine. 4. Rubber containing 59% chlorine. 5. Rubber containing 65.5% chlorine.

In the light of the results already obtained in our investigations, we have again taken up the study of the action of aniline on chlorinated rubbers, with special attention to the study of products containing 34–36 per cent chlorine. In this small range, in fact, important structural transformations take place.

For these measurements, small quantities of chlorinated rubbers were treated with an excess of aniline for a definite time at 100° C and the chlorine displaced by the organic base was determined². The values obtained were used to construct, for each product, a curve representing the percentage of chlorine removed by aniline at 100° C as a function of the time. A study of the curves representing fractions containing 27, 34, 35, 35.5, 39, 44.5, 55, 59, and 65.5 per cent, respectively, of chlorine shows, among the chlorinated rubbers, three principal forms of chlorine (see Figures 4 and 5).

The first form, which is very reactive, continues up to 34–35 per cent chlorine and disappears between 55 and 59 per cent. It probably represents an allylic form of chlorine. The second form, which is very stable, appears toward 35 per cent chlorine and becomes progressively more important to the point of total chlorination. The third form, which is fairly reactive, is present in highly

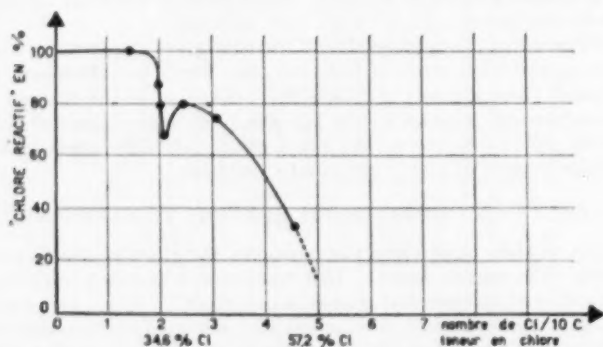


FIG. 6.—Percentage of reactive chlorine as a function of the degree of chlorination. The upper scale of the abscissa indicates the number of chlorine atoms; the lower scale the percentage chlorine content. The ordinate indicates the percentage reactive chlorine.

TABLE 6

Chlorine content (%)	Reactive-chlorine content (%)
27	100
34	87.5
35	80
35.5	68
39	80
44.5	74.5
55	33.5

chlorinated rubbers. It becomes evident from 44.5 per cent chlorine upward. Finally, to avoid any uncertainty hereafter, "reactive chlorine" will refer only to the first form.

It is possible to determine the percentages of reactive chlorine present in the samples studied. The data when plotted as curves (see Figures 4 and 5) show abrupt ascents, then inflections, and, finally become practically linear. It is necessary only to extrapolate to zero time the linear sections of the curves to obtain good approximations of the percentages of reactive chlorine (see Table 6).

Changes of the percentage of reactive chlorine as a function of the chlorine content (see Figure 6) show that rubber, which at the beginning of its chlorination contains only reactive chlorine, undergoes, around 35 per cent chlorine, transformations which involve the transformation of a part of this reactive chlorine to a stable form. From this point on, the percentage of reactive chlorine again increases, passes through a maximum around 40 per cent, and then decreases progressively to zero value between 55 and 59 per cent chlorine.

The product containing 35.5 per cent chlorine is very important, for it marks the end of a structural transformation of the rubber in the course of its chlorination. It is helpful to know precisely its content of allyl chlorine. Now, the percentage of reactive chlorine, determined by aniline at 100° C, does not correspond solely to allylic chlorine; in fact, at this temperature, there take place in partially chlorinated rubbers extensive degradation reactions which may lead to the liberation of a significant amount of chlorine.

In addition to these experiments, the product containing 35.5 per cent chlorine was studied further by subjecting it to the action of aniline, not this

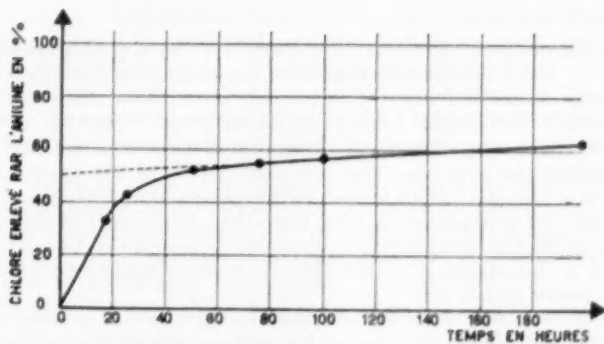


FIG. 7.—Percentage of chlorine removed by aniline from chlorinated rubber containing 35.5% chlorine as a function of the time at 25° C. The abscissa indicates the time in hours; the ordinate the percentage chlorine removed by aniline.

time at 100° C, but at 25° C. At this latter temperature, the degradation phenomena are negligible. The curve in Figure 7, which shows the percentage of chlorine removed by aniline as a function of the time, indicates the true percentage of allylic chlorine, viz., 51 per cent. Knowing that a chlorinated rubber containing 35.5 per cent chlorine contains approximately 2 chlorine atoms per C_{10} group (2.07 precisely), it is obvious that only one of these chlorine atoms is fixed in a stable form. In brief, chlorine unites with rubber first of all by substitution at the allylic position.

Around 34–35 per cent chlorine content (2 Cl/10C), an internal transformation takes place, and one chlorine atom of the two chlorine atoms of allylic form passes to a stable form. Probably the cyclization reactions already referred to are involved, and these reactions lead to the disappearance of one of the two double bonds. As chlorination continues, the content of allylic chlorine again increases, passes through a maximum around 40 per cent combined chlorine, then decreases to zero value between 55 and 59 per cent chlorine.

INSTABILITY OF PARTIALLY CHLORINATED RUBBERS

Up to the point of 50–55 per cent chlorine, chlorinated rubbers are unstable. This instability is particularly evident among products of a relatively low state of chlorination, which, in a period of only a few days, become insoluble, brown, and brittle.

The changes in partially chlorinated rubbers were studied by three methods:

- (1) infrared analysis of films; (2) viscometric measurements of solutions, and (3) studies of the changes of the contents of reactive chlorine.

First of all, a series of samples of partially chlorinated rubbers were subjected to more or less prolonged treatment at 25° and 80° C, and the changes in the spectra resulting from such treatment were determined². In addition, the changes of one of these products in the presence of air and in vacuum were compared by means of infrared analysis. This study led to the conclusion that the progressive changes in partially chlorinated rubbers in the presence of air are the result of two series of reactions, which are independent of each other, and both of which are promoted by heat:

- (1) oxidation reactions, involving degradation and the formation of colored oxidation products;
- (2) intermolecular reactions, leading to insolubilization.

The oxidation phenomena manifest themselves by a general weakening of the spectrum, which is especially notable in the range from 7 to 12 μ , and by an increase of the 6 μ spectral line. This increase seems to be attributable, not to the formation of new double bonds, but rather to the formation of oxidation products, which in many cases show absorption themselves around 6 μ . It is to these oxidation reactions also that we must attribute the appearance of a spectral line around 3 μ . With respect to the intermolecular reactions, they are characterized, for products containing more than 20 per cent of chlorine, by a weakening of the 11 μ spectral line. Since this line seems to be related to the phenomena of cyclization, it follows that the intermolecular reactions proceed at the expense of cyclization.

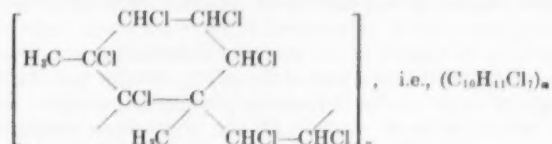
Oxidation reactions and intermolecular reactions, which proceed smoothly in the case of products of low states of chlorination, take place much less readily above 34–35 per cent chlorine. This abrupt increase of stability around 35 per cent chlorine is an indication of a change of structure.

A study by the viscometric method of the aging of partially chlorinated rubbers in solution has led us to the same conclusions. When the phenomena of degradation are manifest by a decrease of the viscosity of solutions, the intermolecular reactions are evident mainly by the formation of a gel phase at high concentrations². However, the progressive changes in partially chlorinated rubbers are much less rapid in solution than in the solid state.

Finally, the aging of partially chlorinated rubbers is manifest also by changes of the content of unstable chlorine. Actually, we have been able to prove, in the study of the reaction of these products with aniline, that, as a result of heat treatment, the percentage of allylic chlorine decreases in lightly chlorinated rubbers and, on the contrary, increases in products containing at least 35 per cent chlorine³. It is probable that lightly chlorinated rubbers, under the influence of heat, undergo a transformation analogous to that which takes place during chlorination when the chlorine content is around 34–35 per cent. With a product which has already been thus transformed, the change is the reverse.

RÉSUMÉ AND GENERAL CONCLUSIONS

The present study is a continuation of the work of Alliot^{1,5} on completely chlorinated rubbers. This latter author has shown that these products, although showing a high degree of molecular dispersion, are homogeneous in chemical constitution, which corresponds to the following cyclic structure:



This constitution involves extensive structural changes during the progress of chlorination.

The present investigation was also devoted to a study of the mechanism of chlorination.

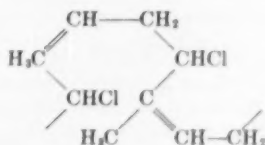
By the fractionation of rubbers of progressively higher chlorine contents, it has been found that, below a chlorine content of 35 per cent (2Cl/10C), these products are highly heterogeneous and that all contain a first fraction containing close to 35 per cent chlorine, as well as fractions of lower degrees of chlorination. Above 35 per cent chlorine, the products are practically homogeneous, although they almost always contain a final fraction which is slightly less chlorinated.

A study of the molecular dimensions by the viscometric method and osmometric method has brought to light the following facts:

- (1) In the initial stage of chlorination, i.e., from 0 to 35 per cent chlorine, there is a very pronounced shortening of the molecular chains;
- (2) Above 35 per cent chlorine, the dimensions of the macromolecules seem to change only insignificantly, but the measurements are complicated by physical phenomena of molecular associations, which are particularly marked between 50 and 57 per cent chlorine.

On the other hand, the analogy between the infrared spectra of cyclohexane and chlorinated rubber containing 35 per cent chlorine must be attributed to this latter product, having a cyclic structure (C_6 rings). The transformation

to another functional group increases the reactivity of each of the two functions. Furthermore, the dichlorinated group will, it is believed, have a pseudocyclic structure:

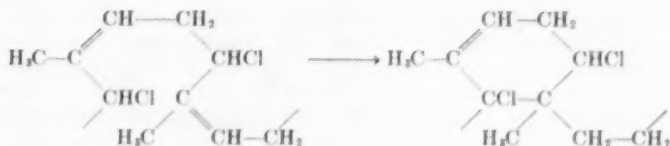


It is to the conversion of the linear form that must be attributed:

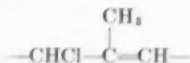
- (1) The notable spectral changes which are evident even before actual cyclization takes place;
- (2) The shortening of the macromolecular chains, indicated by viscometric and osmometric measurements of lightly chlorinated rubbers.

The chain depicted above then reacts with itself, with formation of a true ring.

Because of the mobility of the hydrogen atom, there is, in effect an addition of an α -methylenic C—H group of a reactive group at the activated double bond of the neighboring group. The hydrogen atom fixes itself on the carbon atom of the least substituted double bond, in accordance with the law of Markownikov:



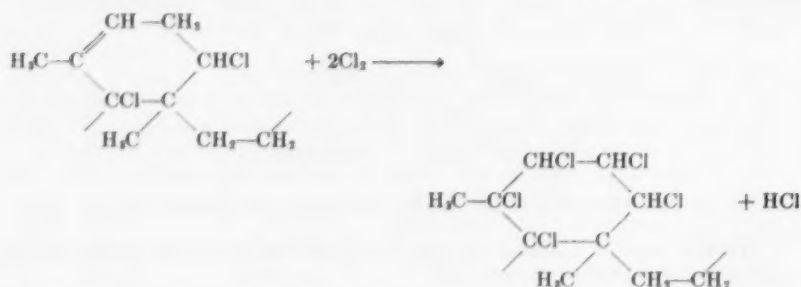
This cyclization is slow in relation to the preceding reaction (fixation of chlorine). It leads to the disappearance of half of the double bonds and, consequently, to the passage of one of the two labile chlorine atoms to a stable form. This results in a notable increase of stability, both with respect to oxidation and to insolubilization. It should be recalled that this insolubilization is brought about by intermolecular reactions which take place particularly easily with lightly chlorinated noncyclized rubbers. In effect, in the solid state and even in concentrated solution, a reactive group:



of a macromolecular chain, instead of reacting with its neighboring chain to form a ring, may react, according to the same process, with a reactive group of a sufficiently nearby chain, with creation of an intermolecular bond. This reaction, like cyclization, reduces the content of allylic chlorine.

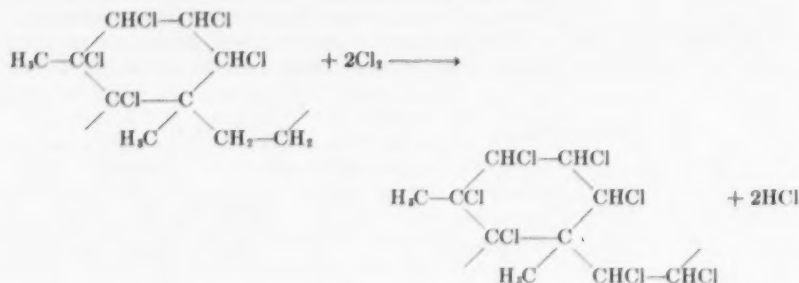
Chlorination may then continue with the cyclized product. Chlorine seems to fix itself simultaneously in α -position to the double bond remaining by substitution and on the double bond by addition. The increase of the percentage of allylic chlorine from 35 to 40 per cent of the total chlorine indicates that, at

the beginning, substitution predominates over addition. In any case, the reaction may be written:

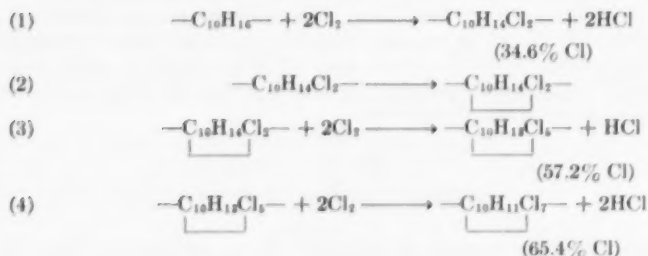


In this compound, containing 57 per cent chlorine, there is no longer any double bond, and certainly no allylic chlorine. This is in good accord with the experimental results.

The final stage of chlorination is a substitution reaction:



Schematically the chlorination of rubber can be written as follows:



Steps (1), (3), and (4), which represent the reactions of actual chlorination, are in accord with the analytical results of Bloomfield¹. Furthermore, this mechanism of the reactions is in fairly good accord with the conclusions of Ramakrishnan, Raghunath, and Pande¹⁴. These authors, in work on the ozonolysis of partially chlorinated rubbers, show the existence of cyclization reactions. However, according to these investigators, these reactions would

take place, for the most part, during the first stage of chlorination and would involve attack by the chlorine by substitution.

CHLORINATION ON THE MACROMOLECULAR SCALE

From the first moment of the action of chlorine on rubber, products containing 34–35 per cent chlorine are formed, and, in addition, products containing much less chlorine and products which are only slightly chlorinated. In other words, we are dealing with macromolecules in which all the C_{10} groups conform to the composition $C_{10}H_{14}Cl_2$, in addition to macromolecules in which only a small number of groups are dichlorinated. Two hypotheses can be advanced to explain this heterogeneity.

(1) The fixation of chlorine on a macromolecule would become progressively easier up to 34–35 per cent chlorine content, on account of the uncoiling of the macromolecule by the action of chlorine atoms which have already been fixed.

(2) Or, according to a hypothesis which seems more plausible, chlorination proceeds by a heterogeneous process, because of the rapidity of the reaction, if for no other reason. The chlorine which enters the reaction mixture would saturate to the point of 35 per cent chlorine content the nearest macromolecules, without attacking the others.

A C_{10} group having fixed two chlorine atoms, cyclization can then proceed. But since this is very slow in comparison with the fixation of chlorine, complete saturation (35 per cent) of a macromolecule would take place before there is any appreciable cyclization. This is the reason that the lightly chlorinated fractions are not cyclized, although they contain saturated groups, and that the fractions containing 34–35 per cent chlorine themselves contain slightly cyclized products.

Chlorination can continue beyond the point of 35 per cent chlorine only under two conditions:

- (1) that the products susceptible of being chlorinated are cyclized;
- (2) that there are no longer any macromolecules containing less than 35 per cent chlorine, fixation of new chlorine atoms taking place preferentially on these latter molecules.

Above 35 per cent chlorine, the rate of chlorination is relatively slow, there should be a good distribution of the chlorine throughout the reaction mixture, and the resulting products should be practically homogeneous.

It should be remarked that rubbers analyzing higher than 35 per cent chlorine, although sensibly homogeneous, all contain a final fraction which is slightly less chlorinated. This fraction is unquestionably composed of the last macromolecules to reach 35 per cent chlorine content, which are not yet cyclized, although chlorination has already proceeded to the point where the major part of the total polymer has become chlorinated. As a result, there is a slight retardation of the chlorination of this last fraction.

SUMMARY

A study of the chlorination of rubber, and of products of its partial chlorination, by physical and chemical methods has made it possible to suggest a mechanism of chlorination.

This mechanism, which is in good accord with the analytical results of Bloomfield, involves cyclization reactions, and thus confirms the cyclized structure of chlorinated rubber which has been attributed by some authors to completely chlorinated rubbers.

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IDENTIFICATION OF CURING AGENTS IN RUBBER PRODUCTS

ULTRAVIOLET ABSORPTIOMETRIC ANALYSIS OF SELECTIVE SOLVENT EXTRACTS *

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Previous published methods used for accelerator identification in compounded rubber products have fallen into four classes: chemical spot-tests or color reactions, precipitation and melting-point tests, chromatography of colored accelerator products, and spectrophotometric identification of chromatographed fractions.

Spot tests or colorimetric methods have been reported for 2-mercaptobenzothiazole and other accelerators¹. Most of these methods were applied to the acetone extracts of large amounts of the rubber compound, and the formula seldom was as complex in softener and antioxidant content as today's commercial products.

The precipitation of guanidine picrates and their identification by melting point have been well developed². Precipitation of thiazoles as the cadmium salts has also been reported³. It has been established in this laboratory that the ultraviolet spectrophotometric method is at least ten times more sensitive than the cobalt oleate spot-test for 2-mercaptobenzothiazole. It has also proved more sensitive and reliable for guanidine identification in today's complex stocks than the picrate melting point method⁴.

Ultraviolet spectrographic techniques have been used by Dufraisse and Houpillart⁵ in following the progress of 2-mercaptobenzothiazole and 2,2'-benzothiazolyl disulfide in the curing of simple rubber products, and Jarrijon⁶ has used the same technique in following the transformation of tetramethylthiuram disulfide to zinc dimethyldithiocarbamate during vulcanization.

Extensive work has been reported by Koch⁷ on spectral absorption and structure of organic sulfur compounds. The ultraviolet absorbance curves of a number of sulfur-bearing materials used as accelerators in the rubber industry are given.

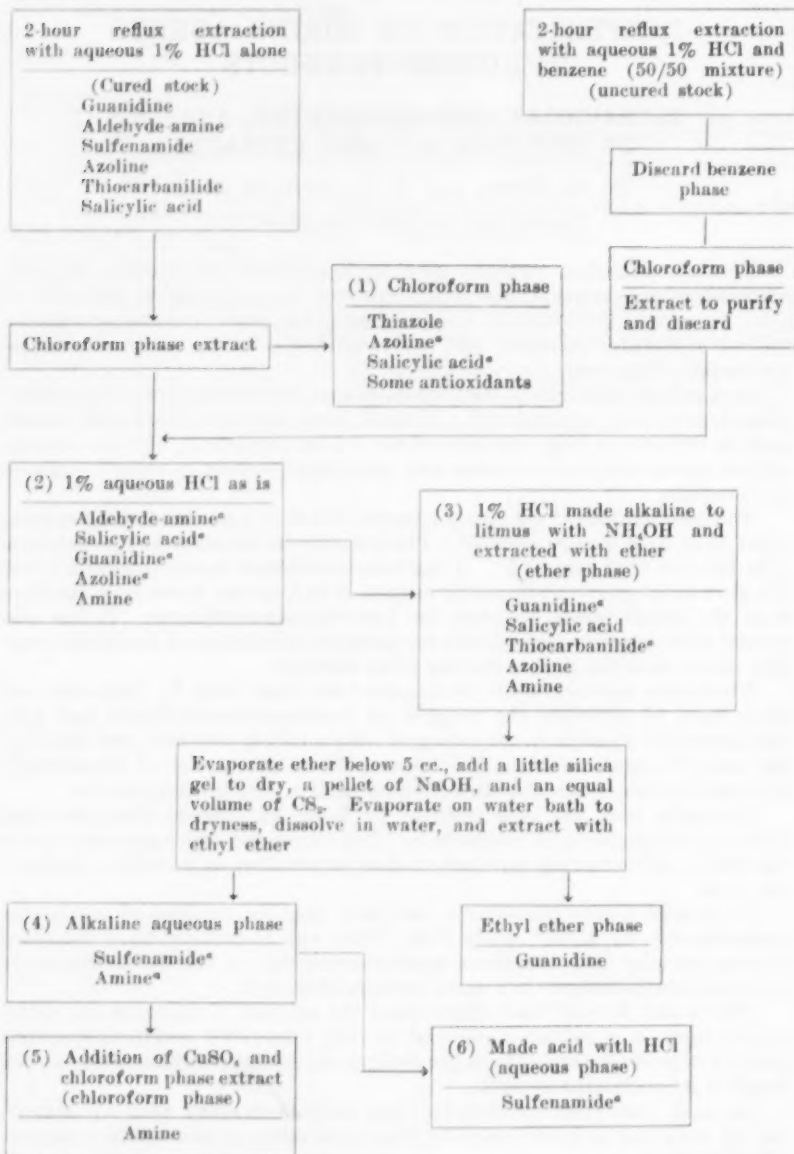
Ultraviolet spectrophotometry has been used for analysis of accelerator masterbatches by Kress⁸, while Fink, Field, and coworkers⁹ have combined chromatography and ultraviolet spectrophotometry in the determination of 2-mercaptobenzothiazole in a cured compounded stock.

Hilton and Newell¹⁰ have determined the amount of thiurams and dithiocarbamates in a rubber compound by the ultraviolet spectrophotometric analysis of products formed from the decomposition of thiocarbamates to carbon disulfide by acidulated alcohol.

Infrared absorption spectroscopy has been successfully used by Mann¹¹, but all work had to be preceded by time-consuming chromatographic separa-

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TABLE I
OUTLINE A. PROCEDURE FOR ACCELERATOR IDENTIFICATION
WITH ACID EXTRACT



* Major or most reliable test. Other tests are more or less confirmatory and are not always needed for identification.

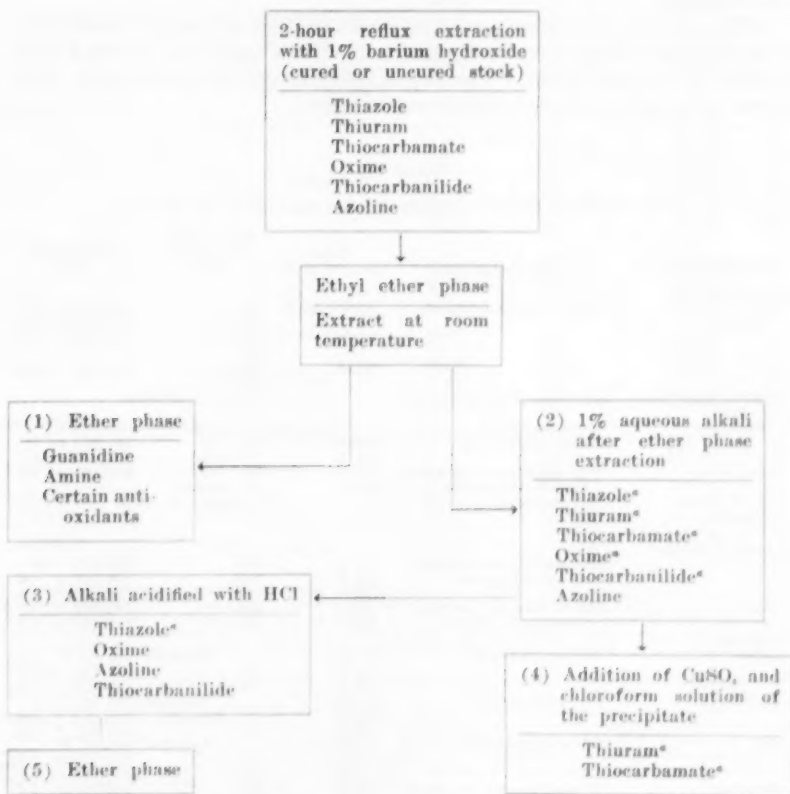
tions. Mann was of the opinion that ultraviolet spectroscopy and polarography were more promising tools than infrared in this respect. Preliminary work using polarographic techniques has been reported for a number of accelerators¹².

In most of the reported techniques for the determination of accelerators involving chromatography, much time is consumed in the initial separation¹², while other methods are not sensitive enough to detect small quantities⁹. Some methods make no allowance for the softeners and antioxidants now commonly incorporated in a rubber compound, which in the case of spot tests could introduce serious errors. Many methods now used require a large quantity of sample which is not always available.

OUTLINE OF METHOD

In the method outlined (Tables I and II), the accelerator is directly and rapidly extracted from the stock, with little interference from other compound-

TABLE II
OUTLINE B. PROCEDURE FOR ACCELERATOR IDENTIFICATION
WITH ALKALI EXTRACT



* Major or most reliable test. Other tests are more or less confirmatory and are not always needed for identification.

ing ingredients. The various classes are identified by matching the ultraviolet spectral curve of the unknown with that of a similar selective solvent preparation of known compounds.

It has been established that guanidines are completely extracted from a compounded, cured stock in as little time as 2 hours⁴, with a much shorter period being required for a qualitative check. Qualitative extraction of other acid- and alkali-soluble accelerators has been made in about the same time. Size of the sample is not a critical factor, and as little as 0.1 gram of stock can be used for the qualitative detection of thiazoles.

A spectral identification of the prepared "fraction" is made, using a Beckman quartz ultraviolet spectrophotometer with the usual 1-cm. quartz cells. Most organic accelerators show some selective absorption in the 220- to 380-m μ region, when the accelerator is dissolved in a suitable solvent (Table III).

Familiarity with the techniques and the spectral curves of the various accelerator fractions from selective solvent extractions enables an analyst to complete a survey for all of the five classes of accelerators in approximately 4 hours. This time could be shortened considerably if a recording instrument were available.

Although this paper is concerned only with qualitative analysis, most of the accelerators mentioned have been quantitatively recovered from different types of cured or uncured stocks. The authors plan to publish quantitative techniques utilizing these basic qualitative procedures.

TABLE III
ABSORBANCE CHARACTERISTICS OF ACCELERATOR FRACTIONS

Trade names	Chemical names	Index no./Solvent ^a	Wave length of maxima, m μ ^b	Absorbance ratio
Aromatic thiazoles MBT, Captax, Thiotax	2-Mercaptobenzothiazole	A1/C; B5/E	329	329/274 = 1.4
			236	329/236 = 1.8
		B2/B	308	232/308 = 1.1
			232	
		B3/A	322	322/232 = 1.8
MBT8, Altax, Thiofide	2,2'-Benzothiazolyl disulfide		Identical with MBT	
Santocure	Benzothiazyl-2-monocyclohexylsulfenamide	A4/B ^d	284, 252	284/252 = 1.1
		A6/A	270, 236	270/236 = 1.1
Nobs, Amax	N-Oxydiethylene benzothiazole-2-sulfenamide	A4/B ^d	286, 262	286/262 = 1.0
OXAF, Zenite Special	Zinc benzothiazyl sulfide	A6/A	No maxima	Identical with MBT
Aliphatic thiazoles Texas	Mixed ethyl and dimethyl mercaptothiazoles	B5/C	326	326/276 = 1.6
		B2/B	298	298/248 = 4.6
		B5/A	318	318/266 = 9.5
		B2/B	294	294/242 = 3.2
		B3/A	314	314/246 = 3.8
Erie	Mixed ethyl and dimethyl thiazolyl disulfides			
Guanidines DPG	Diphenylguanidine	B1/E	Identical with A3/E	
		A2/A	226	226/246 = 1.7
		A3/E	258	258/278 = 1.6
			Identical with A3/E	
		A2/A	254 (shoulder)	254/274 = 0.3
DOTG	Di-o-tolylguanidine	A3/E	254	254/274 = 1.9
TIG	Triphenylguanidine	B1/E	Identical with A3/E	
		A2/E	235	235/226 = 1.02
		A3/E	263	263/284 = 1.4
		B2/B	276	276/250 = 2.8
		A2/A	274	274/254 = 1.8
Permalux	Di-o-tolylguanidine salt of dicatechol borate	A3/E	254	254/274 = 1.9

TABLE III—Continued

Trade names	Chemical names	Index no./Solvent ^a	Wave length of maxima, mμ ^b	Absorbance ^c ratio
Thiocarbamates				
Methyl Zimate,	Zinc dimethyldithio-	B2/B	Identical with methyl Tuads	
Methasate	carbamate	B4/C		
Ethyl Zimate,	Zinc diethyldithio-	B2/B	Identical with ethyl Tuads	
Ethasate	carbamate	B4/C		
Butyl Zimate,	Zinc dibutyldithio-	B2/B	258, 282	258/282 = 1.0
Butasate	carbamate	B4/C	274, 290	274/290 = 1.7
Arazate	Zinc dibenzoyldithio-	B2/B	258, 290	258/290 = 1.1
	carbamate	B4/C	276, 294	276/294 = 2.1
Selenac	Selenium diethyldithio-	B2/B	Identical with ethyl Tuads	
	carbamate	B4/C		
Pip-Pip	Piperidine pentamethylene-	B2/B	258, 282	258/282 = 1.3
	dithiocarbamate			
Thiurams				
TMTD, Methyl	Tetramethylthiuram	B2/B	252, 278	252/278 = 1.0
Tuads, Tuex	disulfide	B4/C	268, 290	268/290 = 1.6
TETD, Ethyl Tuads	Tetraethylthiuram disulfide	B2/B	258, 282	258/282 = 1.0
		B4/C	272, 290	272/290 = 1.6
Monex, Thionex	Tetramethylthiuram mono-	B2/B	Identical with methyl Tuads	
	sulfide			
Aldehyde-Amines				
A-32, 808	Butyraldehyde-aniline	B4/C		
	reaction product	A2/A	242, 322, 280	242/322 = 4.3
		B2/B	228, 280	228/280 = 2.2
Accelerator 833	Butyraldehyde-monobutyl-	A2/A	278	278/242 = 3.7
	amine reaction product	B2/B	278	278/244 = 5.6
Trimens base	Triethyltrimethylenetri-	A2/A	242, 324	242/324 = 3.7
	amine	B2/B	268, 298	268/298 = 1.3
A-19	Acetaldehyde-formalde-	A2/A	237, 314	237/314 = 2.9
	hyde-aniline product			
Asolines				
2-MT	2-Mercaptothiazoline	A2/A	268	268/230 = 5.0
		A1/E, A3/E	268, 248	268/248 = 2.3
		B2/B	246, 264	246/264 = 1.1
		B3/A	268	268/230 = 5.1
NA-22	2-Mercaptoimidazoline	A2/A	268	268/230 = 4.6
		A1/E, A3/E	278, 248	278/248 = 2.2
		B2/B	232	232/252 = 11.3
		B3/A	232	232/252 = 6.2
Special purpose				
Thiocarbamilide		A3/E	240, 288	240/288 = 4.3
		B2/B, B3/A	252	252/272 = 1.4
		B5/E	280	280/246 = 2.3
Aniline		A2/A	240, 280	240/280 = 6.1
Vulcanizing agents				
Dibenzo-GMF	p,p'-Dibenzoquinone-	B2/B	360	360/380 = 3.5
	dioxime	B3/A	314	314/254 = 2.0
		B5/E	313	313/334 = 2.6
GMF	p-Quinonedioxime	B2/B	317	317/336 = 2.0
		B3/A	316	316/336 = 1.9
		B5/E	314	314/334 = 2.7
Activators				
Barak	Dibutylammonium oleate	A4/B ^d	258, 282	258/282 = 1.1
		A5/C	274	274/290 = 1.7
DBA	Dibenzylamine	A4/B ^d	258, 284	258/284 = 1.1
		A5/C	276, 294	276/294 = 1.9
Retarders				
Retarder-W	Salicylic acid	A2/A	236, 304	236/304 = 2.2
		A1/E	236, 306	236/306 = 1.8
E-S-E-N	Phthalic anhydride	A2/A	230, 280	230/280 = 5.5
		A1/E	224, 276	224/276 = 6.4

* Index No. refers to procedure for accelerator identification—either Outline A (acid) or Outline B (base) with the number representing a given block within each outline. Thus, A3/ indicates acid outline, block 3. For the solvent, the following abbreviations apply: A, aqueous alkali; E, ethyl ether; and C, chloroform. Chloroform and ether may usually be used interchangeably. Where chloroform is used in place of ether, the wave length of the maximum will be shifted about 2 mμ toward the longer wave-length region.

^b Primary or most characteristic maximum listed first. In a few cases the secondary maximum is no more than a "shoulder", but it is characteristic.

^c Ratio of absorbance of strongest and next most intense maximum where two maxima are present. Represents ratio of maximum to adjacent minimum where single maximum is present. If no minimum is present, ratio is that of maximum absorbance to an arbitrarily selected wave length 20 mμ toward longer wave-length region. Purpose of ratio is to indicate selectivity or sharpness of maximum, which is important for identification. Ratio given is believed reasonably accurate, but may be expected to vary somewhat depending on purity and amount of interference in extract.

^d Barium salts are represented in all alkaline solutions except for (A4/B)^d, where absorbance reported is that of sodium salt. Prepared thiocarbamate derivatives of sulfenamide and amine activators are sodium salts.

EXTRACTION PROCEDURE

Alkali.—The stock to be used for analysis is thoroughly milled and sheeted thinly in a cool mill, and 1 to 2 grams is added to a ground-glass-jointed Erlenmeyer flask. The sample is refluxed in about 50 ml. of 1% barium hydroxide, with the flask connected to a condenser fitted with a ground-glass tapered joint. The hot solution, when filtered and cooled, is ready for the spectral analysis indicated in Table II.

Before a spectral analysis is made, the solution should be liquid-liquid extracted with chloroform or ethyl ether to remove small amounts of dissolved antioxidants and softeners, which are known to be present in the hot alkaline

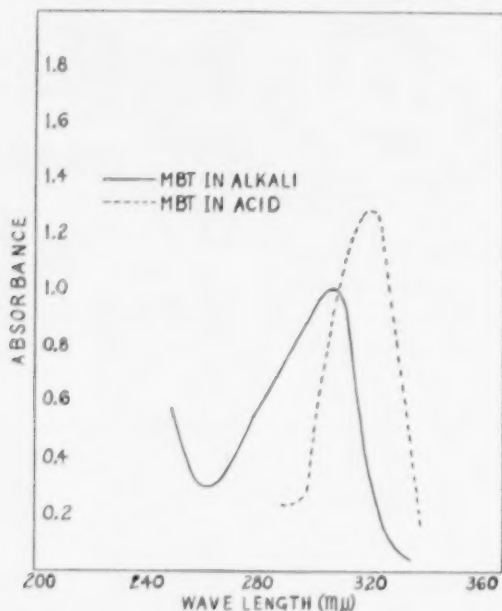


Fig. 1.—Thiazoles in aqueous barium hydroxide and hydrochloric acids solutions.

solution but which are only slightly soluble on cooling. Guanidines may also be qualitatively identified in this ethyl ether extract, if they are present alone or in large quantities.

Acid.—The procedure is identical to that for the alkali extraction, with the exception of the solvent. Here approximately 50 ml. of 1% hydrochloric acid are used if the stock is cured and an additional 50 ml. of benzene if an uncured stock is being analyzed. If benzene has been used, the benzene is removed after cooling and the acid solution boiled for a few minutes to remove any traces of benzene. At this stage the acid solution is ready for any special preparation which may be required for the complete analysis.

Thiazoles will be extracted from the aqueous acid by the initial ethyl ether phase extraction, but as they are best determined in the alkaline extract, they may be considered as interference here.

AQUEOUS ALKALI EXTRACT

Aromatic thiazoles.—Aromatic thiazoles are characterized by a maximum found in the alkali at 308 $m\mu$. This is the barium salt of mercaptobenzothiazole. Substituted thiazoles, such as *N*-oxydiethylene benzothiazole-2-sulfenamide or benzothiazyl-2-monocyclohexylsulfenamide will exhibit this same maximum, for the alkali causes the molecule to split and yields the characteristic thiazole salt. When the alkaline solution is made acid to litmus, the maximum shifts to 322 $m\mu$ (Figure 1), which represents the absorption associated with mercaptobenzothiazole itself.

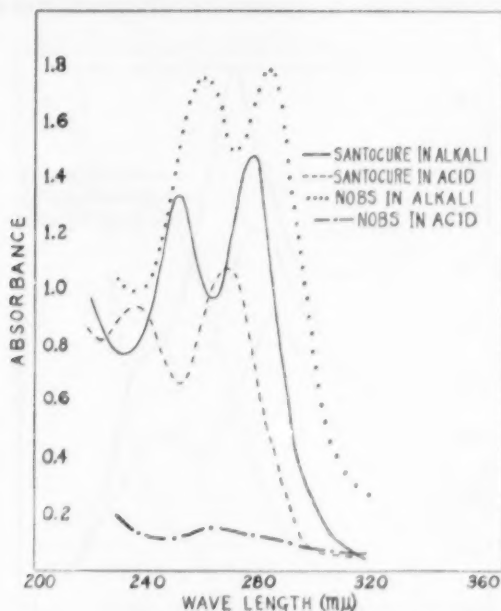


FIG. 2.—Thiocarbamate derivatives of sulfenamides in aqueous sodium hydroxide and hydrochloric acid.

Aliphatic thiazoles.—The commercial aliphatic thiazoles, Texas and Erie, which are mixed ethyl- and dimethylmercaptothiazoles, also exhibit a gradual shift in location of absorbance maximum as the pH is varied. Texas, in a solution alkaline to litmus, shows a relatively symmetrical maximum at 298 $m\mu$, with a shift to 318 $m\mu$ when the solution is made acid to litmus. Erie in alkaline solution has a maximum at 294 $m\mu$, and, when acidified, the maximum is located at 314 $m\mu$. The 4- and 14- $m\mu$ difference in location of maxima in acid and base serves to differentiate the aromatic and aliphatic thiazoles.

The presence of a thiazole is further confirmed by acidifying the aqueous alkaline solution with concentrated hydrochloric acid and extracting with ethyl ether. The ether phase gives a spectral curve similar to that in aqueous acid, but with the maximum at 326 $m\mu$. This is the normal absorption curve for 2-mercaptobenzothiazole in an organic solvent.

Because of the formation of 2,2'-benzothiazolyl disulfide when 2-mercapto-

benzothiazole is used in a compounding formula, or vice versa, depending on the conditions of vulcanization, it cannot be determined which aromatic thiazole was added. It is also known that zinc salts of the thiazoles may be formed under the conditions of vulcanization where zinc oxide is present, if either 2,2'-benzothiazolyl disulfide or 2-mercaptobenzothiazole has been used. Here, the thiazole will be found as 2-mercaptobenzothiazole alone, and not as the individual 2,2'-benzothiazolyl disulfide or zinc mercaptobenzothiazole.

Thiocarbamates.—The alkaline solution contains added thiocarbamates and any thiocarbamates which have been formed by the action of zinc oxide and thiurams during vulcanization, or during the extraction by the alkali itself. Absorbance of thiocarbamates in aqueous alkali (Figure 2) is as characteristic

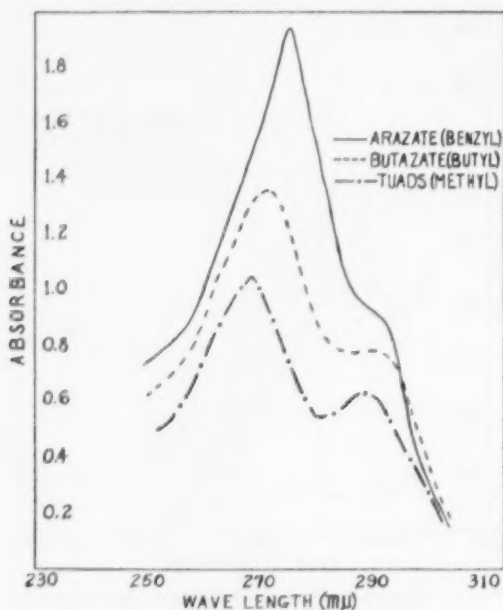


Fig. 3.—Copper complex of thiurams and thiocarbamates in chloroform.

as that of the copper salt in chloroform, but is subject to greater interference from other alkali-soluble accelerators, particularly thiazoles. If thiazoles are absent from a stock, then identification can be made in the alkali alone, without resorting to formation of the copper complex.

Positive identification of the type of thiocarbamate can be made here by precipitating any thiocarbamate with 1 per cent copper sulfate solution. The resulting deep brown copper thiocarbamate precipitate, soluble in chloroform, is a positive test for the presence of the thiocarbamate. (If a brown precipitate is formed which is insoluble in chloroform, free sulfur is most probably present in the stock in rather large quantities.) The thiocarbamate is identified by a spectral check of the copper complex in chloroform (Figure 3). Here distinct double maxima are found at positions dependent upon the structure of the thiocarbamate formed. The location of the maximum at the shortest wave

length increases altogether about 8 μ , and the prominence of the secondary maximum is reduced as the molecular weight of the attached group increases through methyl, ethyl, butyl, and benzyl groups.

Thiocarbamates also react with many ions other than copper to yield white or colored complexes which show selective absorbance in the ultraviolet region. Nickel or cobalt salts give a thiocarbamate, with a spectral curve distinctly different from that of the copper complex. The difference is so pronounced that sodium diethyldithiocarbamate has been used for spectrophotometric detection of copper, cobalt, and nickel simultaneously¹⁴. However, copper appears to be as good as any metallic ion tested for the purpose of distinguishing the different thiocarbamates.

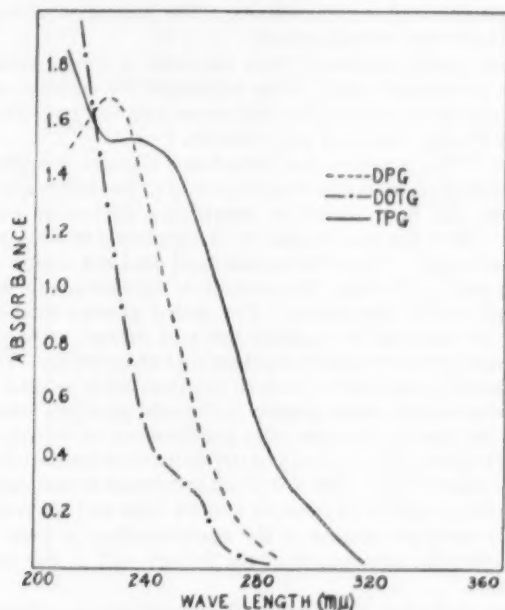


FIG. 4.—Guanidines in aqueous 1 per cent hydrochloric acid.

Thiurams.—Thiurams are normally extracted by the aqueous alkali as the thiocarbamate derivative. It is not possible to distinguish tetramethylthiuram monosulfide from tetramethylthiuram disulfide in a cured stock, since both are normally converted partially or almost completely to their zinc thiocarbamate salts. The absorbance curve of tetramethylthiuram monosulfide itself in an organic solvent is distinctly different from that of tetramethylthiuram disulfide, and identification is simple if the accelerators are recovered in their original form. If the stock is uncured, much of the soluble tetramethylthiuram monosulfide can be extracted with distilled water, in which tetramethylthiuram disulfide is essentially insoluble. As with thiocarbamate accelerators, the copper complex will distinguish between ethyl and methyl thiurams.

AQUEOUS ACID EXTRACT

Guanidines.—The guanidines, being alkaline materials, are found in the acid phase after extraction with ethyl ether to remove any thiazole. The curve of the guanidine hydrochloride in acid is characteristic for triphenylguanidine, diphenylguanidine, and di-*o*-tolylguanidine (Figure 4). Confirmatory identification of the type of guanidine is carried out by making the acid extract strongly alkaline to litmus with ammonium hydroxide and extracting this alkaline solution with ethyl ether. Each of the three types of guanidines mentioned here give a characteristic single maximum which is the same as that of the individual guanidine accelerator in an organic solvent.

It is also possible to determine the presence of a guanidine material in such compounds as diphenylguanidine oxalate and diphenylguanidine phthalate, which are substituted diphenylguanidines. The guanidine component of the molecule is normally determined as such.

Guanidines are easily separated from thiazoles in stocks where they occur together by the preliminary ethyl ether extract of the aqueous acid stock extract. It is advisable to extract the acid phase two to three times with ethyl ether to remove the last traces of any thiazole.

Sulfenamides.—The presence of a substituted thiazole or sulfenamide, such as *N*-oxydiethylene benzothiazole-2-sulfenamide or benzothiazyl-2-monocyclohexylsulfenamide, can be detected by identifying the amine associated with this compound. Here the acid breaks up the molecule to form a thiazole and an amine hydrochloride. Since the amine itself does not absorb selectively, it is treated with carbon disulfide to produce a thiocarbamate which exhibits characteristic ultraviolet absorption. The amine present in the acid extract of a stock can be removed by making the acid extract strongly alkaline to litmus with sodium hydroxide and extracting with chloroform. The chloroform is evaporated carefully on a water bath to less than 5-ml. volume. To this are added one pellet of solid reagent sodium hydroxide, an equal volume of carbon disulfide, and a few pieces of coarse silica gel to ensure as anhydrous a solution as possible. (The preparation should be dry to prevent formation of interfering carbon disulfide absorbance at 308 to 312 μ attributed to xanthate formation.) The mixture is evaporated to dryness on a water bath and the residue dissolved in water. Ultraviolet absorbance of the aqueous alkali is then recorded. It will show characteristic absorbance of the sodium salt of the particular thiocarbamate present.

Confirmation of the type of sulfenamide present can be obtained by acidifying this alkaline solution. If benzothiazyl-2-monocyclohexylsulfenamide is present, two maxima are observed at approximately the positions of the two minima in the alkaline solution (Figure 2). *N*-oxydiethylene benzothiazole-2-sulfenamide presents a spectral curve in the alkaline solution similar to benzothiazyl-2-monocyclohexylsulfenamide, but with maxima at different wave lengths. Making the solution acid to litmus will destroy any strongly selective absorbing material, thus differentiating *N*-oxydiethylene benzothiazole-2-sulfenamide from benzothiazyl-2-monocyclohexylsulfenamide. The absorbance of the acidified solution is unstable and should be recorded immediately.

If copper sulfate is added to a part of the alkaline solution, a brown precipitate soluble in chloroform is further proof of the presence of thiocarbamates. Spectral absorbance here will aid in identification of an amine added as such originally. Any amine residue from thiocarbamates or thiurams added to the stock and decomposed by the acid may be expected to appear here. However,

absorbance characteristics are sufficiently different so that sulfenamides may be identified by this procedure.

Aldehyde-Amines.—Aldehyde-amines will be found in the aqueous acid extract of a cured, compounded stock after the initial ethyl ether extraction. If aromatic amines and certain aliphatic aldehyde-amines are present, the spectral curves in aqueous acid are usually characteristic enough for identification, where thiazoles and guanidines are absent (Figure 5). If thiazoles are present, they will be removed by ethyl ether extraction, leaving the characteristic absorbing material associated with the amine in the acid extract. By following the outlined procedure and preparing thiocarbamate derivatives, the common aliphatic amines may also be detected. It should be noted that sulfur vulcanization of a rubber compound with an aldehydeamine may yield a trace

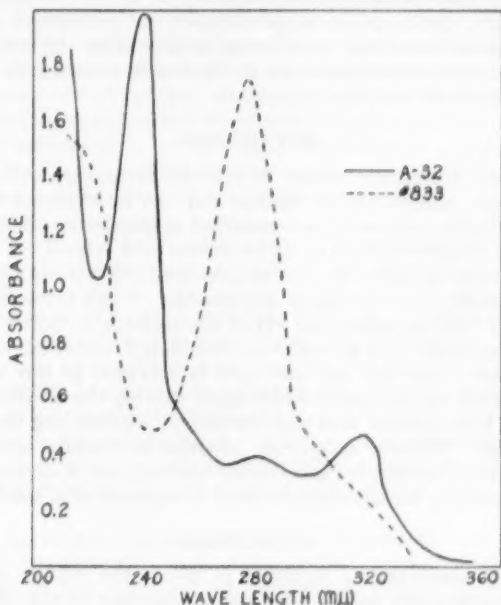


Fig. 5.—Aldehyde-amines in aqueous hydrochloric acid.

of a thiocarbamate residue. If an aldehyde-amine is detected as such in considerable quantity, and only a trace of a thiocarbamate is present, it is probable that the thiocarbamate was formed from the amine during vulcanization.

SPECIAL PURPOSE ACCELERATORS

There are a number of special purpose accelerators which can be detected in the alkali and acid extracts of cured compounded stocks.

Oximes.—A stock accelerated with *p,p'*-dibenzoquinonedioxime shows a maximum in alkali at 361 mμ, while the maximum in the same solvent for *p*-quinonedioxime is found at 317 mμ.

Azolines.—The presence of 2-mercaptothiazoline can be detected by the sharp maximum found in alkali at 246 mμ, with a shoulder at 264 mμ. Acidi-

fication of the alkaline solution gives a single symmetrical maximum at 268 $m\mu$. 2-Mercaptoimidazoline can be differentiated from 2-mercaptothiazoline by the single maximum in alkali at 232 $m\mu$. No change is observed when this solution is acidified.

Thiocarbanilide.—This exhibits a broad maximum at 252 $m\mu$ in alkali and in the alkali extract after it is made acid. Ethyl ether phase extraction of the acid gives the normal single 280- $m\mu$ maximum of this material in an organic solvent.

Xanthates.—Little work has been done with xanthates, but the commercial compound dibutylxanthogen disulfide exhibits selective absorption in alkali solution with maxima at 226 and 302 $m\mu$. If the xanthates do not decompose completely during curing, it is believed that some qualitative detection could be made. Identification would be more certain if an uncured sample were used.

Several other special purpose accelerators not mentioned here will give characteristic absorbance curves at some point, using the method outlined. Any new accelerators which are acidic or alkaline in nature may be expected to fit into this scheme of analysis.

RETARDERS

Retarders are sometimes added to prevent premature vulcanization of a stock. They are usually acid in nature and can be detected along with accelerators. Salicylic acid could be considered as interference in the detection of guanidines and thiazoles with the hydrochloric acid extract. The characteristic double maxima of salicylic acid at 236 and 306 $m\mu$ are observed in the aqueous acid itself, when thiazoles are absent. When present, the thiazoles are removed by first adjusting the pH of the solution to between 8.5 and 9.0. It has been determined that thiazoles are completely extracted with ethyl ether in this pH range, but that salicylic acid is retained in the aqueous alkali. Salicylic acid itself can be identified by again making the alkaline solution acid to litmus with hydrochloric acid and liquid-liquid extracting the salicylic acid with ethyl ether. Phthalic anhydride (changed to phthalic acid by the action of the solvent) may be detected in a similar manner, and is readily distinguished from salicylic acid by its absorbance curve in aqueous acid solution.

ACTIVATORS

Some of the compounding formulas in use in the rubber industry at the present time employ the use of an organic activator of the amine type. If present in a stock, these will be extracted with 1 per cent hydrochloric acid, and their presence can be determined following Table I, with particular attention to the blocks concerning the identification of amines.

DISCUSSION

Selective solvent extraction coupled with ultraviolet spectrophotometry offers a strong tool for the identification of many alkaline and acidic organic materials when present in trace amounts in natural or commercial products.

It is generally agreed¹¹ that ultraviolet spectrophotometry is more sensitive than infrared. This is of particular value in the identification of trace amounts of rubber compounding materials, such as accelerators and antioxidants, which are usually put into a compounding formula in quantities of 1 per cent or less.

Infrared may be more specific than ultraviolet in distinguishing between similar accelerators. However, it has been shown here that similar compounds

can often be converted by simple chemical treatment to give distinctly different ultraviolet absorbance characteristics which will readily identify them. The short spectral range of ultraviolet also makes for more rapid identification. Where applicable, the 0.12-micron range of 220 to 340 $m\mu$ in the ultraviolet gives as positive identification of most common rubber accelerators as does complete coverage of the 1- to 14-micron range of infrared.

The tedious chromatographic isolation of accelerators usually recovers the accelerator as the compound or compounds present in the stock. This has both advantages and disadvantages. Chromatography, coupled with ultraviolet and infrared spectroscopy, may be the ideal method for the identification of accelerator reaction products in a cured stock. Many accelerators are converted partially or entirely during vulcanization to different compounds. Therefore, identification of a single added accelerator by chromatography may mean isolation of two to four compounds, which might confuse matters as to which material was added originally. Thus a tetramethylthiuram disulfide cured stock may have tetramethylthiuram disulfide, zinc dimethyldithiocarbamate, or tetramethylthiuram monosulfide present. A benzothiazyl-2-monocyclohexylsulfenamide cured stock may have the original benzothiazyl-2-monocyclohexylsulfenamide, 2-mercaptobenzothiazole, 2,2'-benzothiazolyl disulfide, and traces of cyclohexylamine or thiocarbamate, formed from the cyclohexylamine. Aldehyde-amine accelerators may leave traces of thiocarbamates on curing.

The rapid selective solvent extraction of accelerators outlined here will often convert accelerator breakdown products in a cured stock to a single material of known composition. This fact, and the use of aqueous solutions to eliminate interference of such materials as softeners, presents a practical procedure for the identification of general classes of accelerators.

Though barium hydroxide is used here, the solvent could just as well be sodium or potassium hydroxide, or sodium sulfite in many cases. Also, ethyl ether used for some phase extractions and as a solvent for ultraviolet absorbance might be replaced by chloroform. Chloroform is a stronger solvent and is nonflammable, but ether is usually preferred because chloroform does not transmit ultraviolet below 246 $m\mu$, whereas ethyl ether transmits to about 220 $m\mu$.

One factor working in the analyst's favor is the fact that accelerators which might possibly interfere with each other in the proposed method of analysis are rarely used in the same rubber compound. Thus, thiocarbamate and aldehyde-amine accelerators are both considered fast curing, and are not commonly used together in rubber products. As sulfenamides are used primarily where scorching is a problem, no ultra-accelerators such as amines or thiocarbamates will be used in the same stock. Also, common practice dictates that where more than one accelerator is used, a combination of an acidic thiazole with an alkaline guanidine, thiuram, or amine is normal procedure.

Therefore, this method of selective solvent extraction to separate alkaline and acid materials fits in well with present-day rubber compounding practices.

SUMMARY

A method has been devised for identification of organic compounds that accelerate the vulcanization of rubber products. Identification of these active trace materials aids product improvement and quality control. Identification is made through ultraviolet spectrophotometric absorbance curves over the 220

to 380 $m\mu$ region on the aqueous alkali or acid extracts, or on liquid-liquid ethyl ether extracts of the aqueous solutions. Thiazole, thiuram, thiocarbamate, amine, and guanidine classes of commercial accelerators are regularly identified in 2 grams of uncured or cured rubber products, with less than 4 hours' elapsed time. Interference of common softeners and antioxidants is usually negligible. The method is more rapid than chromatographic procedures and more sensitive and specific than spot-test methods. Quantitative results may be obtained if calibration work is undertaken.

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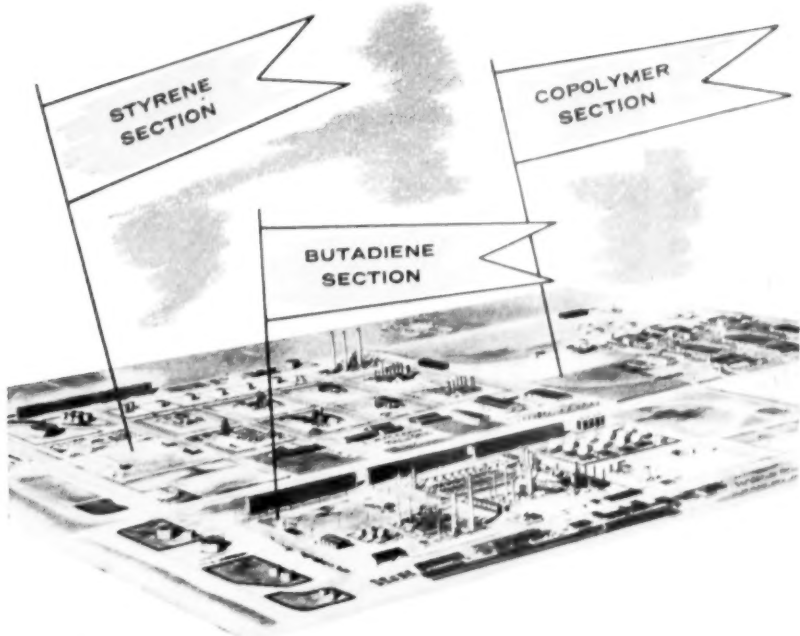
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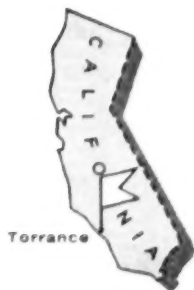
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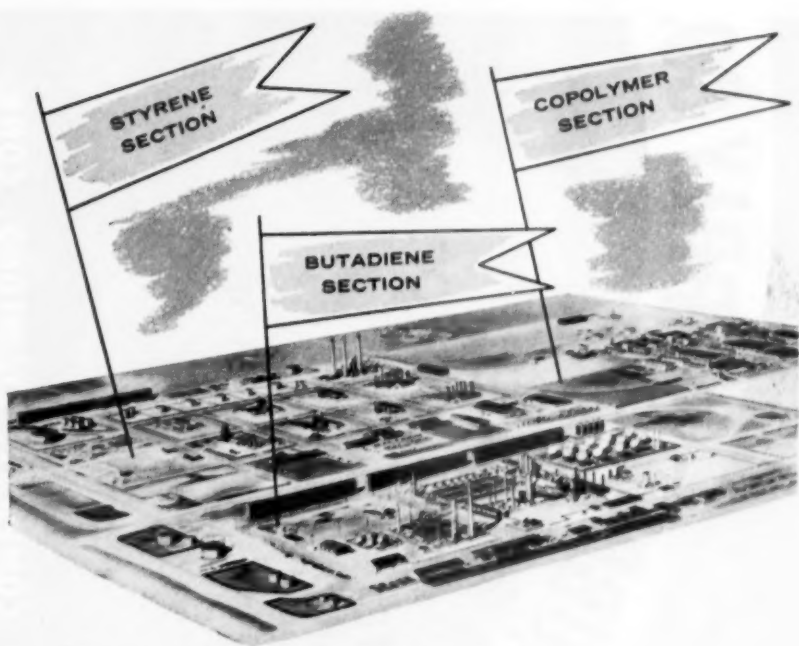
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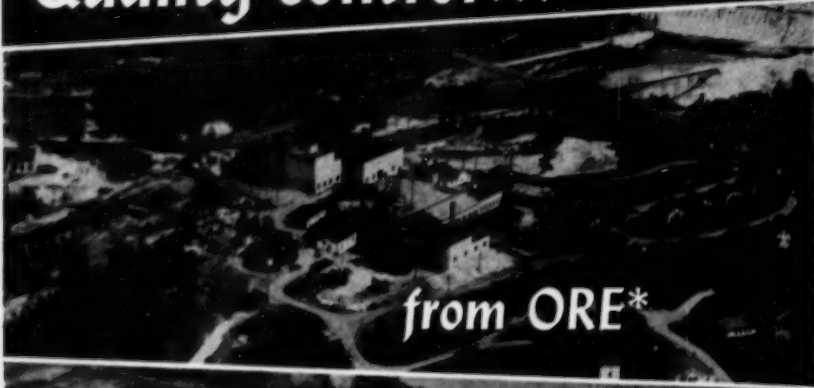
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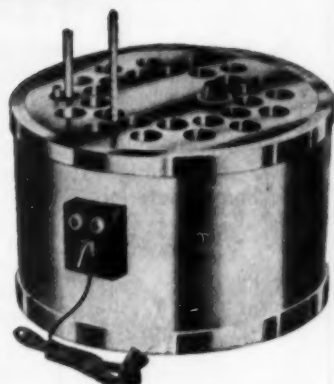
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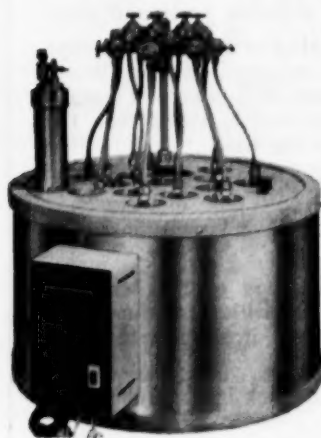
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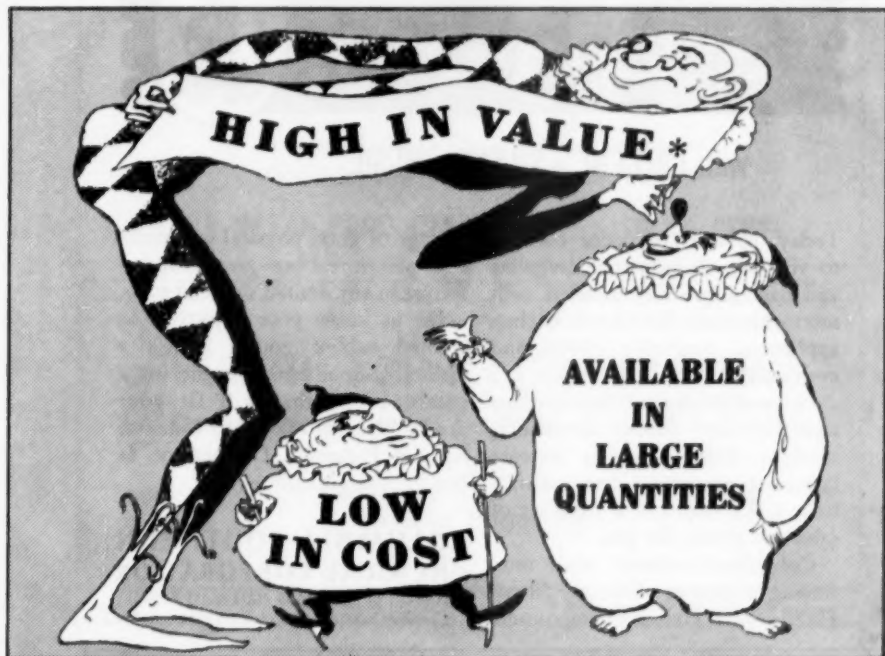
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